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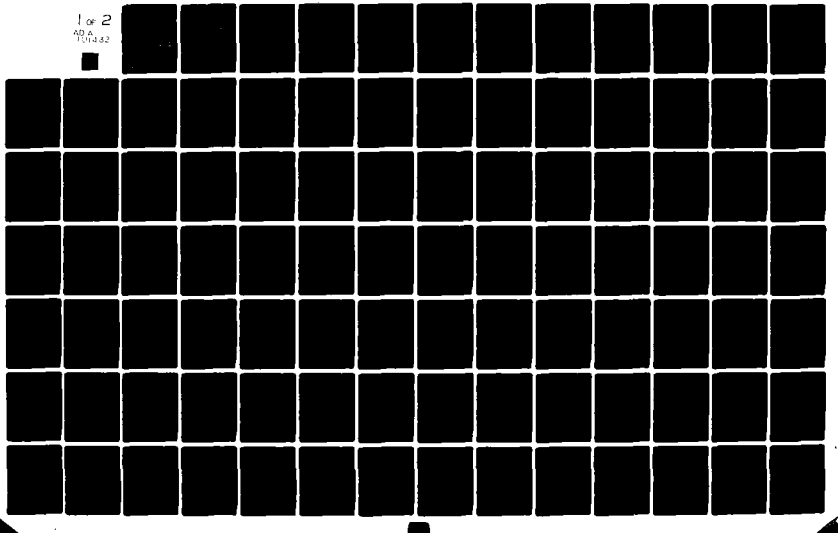

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Laser Photochemistry

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This is a general review dealing with experimental and theoretical aspects of laser photochemistry in the gas phase and condensed phases. The review is divided into two main sections: (1) spectroscopy and (2) molecular interactions and reaction dynamics. Topics covered under spectroscopy include single-photon and multiphoton processes, classical and quantum models, and selective (nonthermal) and thermal effects. The section on molecular interactions and reaction dynamics considers the interaction of intense radiation with gas-phase collision dynamics. In the liquid phase, the topics covered

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include laser light scattering, laser-induced chemical reactions and time-resolved studies using ultrashort laser pulses. In connection with the solid phase, attention is given to selective and thermal excitation and the role of multiphonon couplings, heterogeneous catalysis, and chemical vapor deposition and annealing with applications to microelectronics fabrication.

LASER PHOTOCHEMISTRY

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I. Introduction

The phenomenon of "light amplification by stimulated emission of radiation" (the laser), discovered around two decades ago, has had a significant influence on the research programs of the physical, engineering and biological communities. While the major effort has been in laser development, recently a variety of laser applications have been explored, such as the use of lasers as scalpels in surgery, as means of communication by fiberoptics and as components in programs of nuclear energy development. The application of lasers in chemistry is still in the early stages, and while this has been generally confined to basic research projects, it appears that such application is beginning to see practical advantages in government and industry.

The organization of this review is divided into two sections apart from this introductory section (Section I). Section II deals with spectroscopy, and Section III deals with molecular interactions and reaction dynamics. The distinction between these two sections parallels the manner in which chemical research has historically been carried out. Spectroscopists tend to be concerned with the interaction of light with matter (i.e., molecular systems) as a topic of interest in itself, where the concern for dynamical processes exists only in how they modify such interaction. On the other hand, researchers in molecular interactions and reaction dynamics either have ignored problems in which a molecular system interacts with an

external radiation source or have viewed such a source as just a modifier or disturbance on the dynamics of interest. Exceptions to this distinction can certainly be found, particularly in the area of photochemistry. In fact, the availability of lasers has begun to erase this distinction in many laboratories; i.e., many chemists are now interested and active in both the areas of spectroscopy and molecular dynamics. Nevertheless, this distinction still serves as a useful guideline for presenting a review of photochemistry in 1981.

II. Spectroscopy

In this section we discuss a variety of laser-induced processes which serve to illuminate the structure of atomic and molecular species. By structure we mean chiefly the distribution of quantized energy levels (or states) in a system--electronic, vibrational and rotational, and the extent to which these can be made to interact with each other via the radiation field. We hope to demonstrate here that an external radiation field, such as a laser, besides being useful as a probe of structure, may also be essential in altering structure to suit our needs. This latter aspect of the radiation field will be revealed in the section on chemical dynamics. Here we will focus on the former aspect, as well as on the versatility of the laser as an agent to selectively state-prepare specific chemical species. This last function is of enormous importance from the viewpoint of chemistry since certain reactions will occur only when the

reagents are in specific states. Herein lies the claim (as yet unrealized) that laser photochemistry may fulfill the age-old dream of alchemy.

It is useful to distinguish between two types of laser-induced processes: single-photon and multiphoton. A single-photon process can be either a single-step or multistep process involving a single photon in each step, and the photons in the different steps may come from different lasers. A multiphoton process, on the other hand, involves a number of photons (may be as high as 30) in a single step. This distinction will be classified by examples in what follows.

A. Single-Photon Processes.

Functioning as a probe or preparation agent, the laser is essential in the following processes: photoionization, photodissociation, photoisomerization and photodeflection, among others. The first two of these have been the most widely studied, and we will address them chiefly.

The difference between atomic and molecular systems in laser photoprocesses is that atoms in general present much more stringent resonance requirements. In other words, the energies of the laser photons have to match up quite well with those of the atoms. This is due to the fact that there is only one kind of excitation in atoms -- discrete electronic excitations. Molecules, on the other hand, are much less selective because, in addition to electronic excitations, they exhibit excitations

due to nuclear motion, namely, vibrational and rotational excitations. This leads to much more complex spectra which can "accomodate" photons of widely varying energies. In general, electronic transitions correspond to photons in the visible and ultraviolet (UV) range, vibrational transitions to the infrared (IR) range, and rotational transitions to the microwave range. Laser photochemistry is thus mainly concerned with electronic and vibrational transitions. (In this discussion we will ignore the effects of the rotational states on these transitions.) There is another very important feature in molecular systems which helps to relax the resonance requirements on laser photons. This is the Born-Oppenheimer adiabatic (slow) variation of electronic energy levels with nuclear separation. In situations where *electronic states do not support bound levels*, the electronic energies vary continuously as the nuclei in a molecular system move with respect to each other, and resonance requirements (at least over a certain range of frequencies) can be relaxed accordingly. This relaxation of resonance requirements due to nuclear dynamics forms the cornerstone of laser-induced dynamical processes (both reactive and nonreactive).

With respect to atoms, selective multistep photoionization is the most interesting and potentially useful photophysical process made possible by lasers, the most attractive application being laser isotope separation (LIS). All selective ionization schemes for atoms involve the following sequence of processes: 1) selective excitation; 2) ionization of the excited atoms. Fig. 1 illustrates two typical schemes which are frequently

employed in LIS: (a) represents a scheme in which the second laser (with photon energy $\hbar\omega_2$) brings the atom to an autoionizing state. (An autoionizing state is a configuration of discrete electronic energy where two electrons are excited, with the discrete energy level higher than the ionization limit of the valence electron.)

An example of process (a) is the ionization of Rb by a dye laser tuned to ω_1 = 7947.6Å (Ambartzumian and Letokhov, 1972). This photoexcites the 5p $^2P_{3/2}$ state of Rb. A second photon of ω_2 = 3471Å which is generated by the second harmonic of the same laser, then brings the excited state to the continuum:

$$\text{Rb(vapor)} + \hbar\omega_1(7947.6\text{Å}) \rightarrow \text{Rb}(5p\ ^2P_{3/2}) \xrightarrow{\hbar\omega_2(3471\text{Å})} \text{Rb}^+ + e$$

A second example of this process is the LIS of ^{235}U (Tuccio et al., 1975):

$$^{235}U + \hbar\omega_1(3781\text{Å}) \rightarrow {}^{235}U^* \text{ (low-lying metastable state at 620 cm}^{-1}\text{)} \xrightarrow{\hbar\omega_2\begin{pmatrix}3075\text{Å}\\3564\text{Å}\end{pmatrix}} U^+ + e.$$

An example of process (b) is the two-step selective autoionization of Ca (Brinkmann et al., 1974). Ca atoms are prepared in the metastable states 4s4p $^3P_{2,1,0}$, which are then excited by a first laser (ω_1 = 6162Å) to the excited state 4s5s $^3S_1$. A second photon (ω_2 = 4880Å) subsequently further excites the atom to

the autoionizing state 3d5p $^3P_1$:

$$\begin{array}{lll} Ca(4s4p\ ^3P_{2,1,0}) + \hbar\omega_1(6162\mathring{A}) & \rightarrow & Ca(4s5s\ ^3S_1) \\ & & \downarrow \hbar\omega_2(4880\mathring{A}) \\ & & Ca(3d5p\ ^3P_1) \rightarrow Ca^+ + e. \end{array}$$

For molecular photoionization we can mention the single-step ionization of O_2^- (Cosby et al., 1975) and the two-step ionization of formadehyde (Andreyev et al., 1977):

$$O_2^- + \hbar\omega \rightarrow O_2 + e\ ,$$

$$\begin{array}{lll} H_2CO(X^1A_1) + \hbar\omega_1(3371\mathring{A}) & \rightarrow & H_2CO^*(^1A_z) \\ & & \downarrow \hbar\omega_2(1600\mathring{A}) \\ & & H_2CO^+ + e. \end{array}$$

Let us now turn to the topic of selective multistep photodissociation of molecules. As mentioned before, the spectroscopy of molecules is much more complex and interesting than that of atoms due to the presence of the nuclear degrees of freedom. This extra complexity provides the opportunity for a judicious combination of IR and UV (or visible) lasers for effecting the dissociation process. Hence selectivity can be considerably enhanced. Fig. 2 illustrates two important schemes of selective multistep photodissociation, which are also of great potential value for LIS. Fig. 2(a) represents the process of two-step photodissociation: the first laser provides an IR photon exciting a high vibrational level of the ground electronic state, and a second laser with a UV photon then accesses the repulsive

excited electronic state, which causes the molecule to dissociate. This process can be considered the molecular analog of atomic selective two-step photoionization [Fig.1(a)]. Fig. 2(b) represents the process of single-step selective laser-induced predissociation: a UV laser excites the molecule to an excited vibrational level in an excited electronic state which crosses a repulsive excited electronic state. By virtue of the crossing, vibrational motion in the bound electronic state is coupled to continuum motion in the repulsive state, thus allowing dissociation to take place. (A dissociation of this type as a result of curve crossing, whether induced by laser radiation or not, is known as predissociation.)

We now proceed to some examples. For a prototype of two-step photodissociation, we mention the process (Letokhov,1973):

$$HCl(X^1\Sigma^+,\ v = 0) + \hbar\omega_1(1.19\mu m) \rightarrow HCl(X^1\Sigma^+,\ v = 3)$$

$$\downarrow \hbar\omega_2(2650\text{Å})$$

$$HCl(A^1\Pi) \rightarrow H + Cl$$

In this example, the ground electronic state of HCl, $X^1\Sigma^+$, supports a number of vibrational levels. The first-laser, supplying an IR photon of wavelength 1.19μm, excites the system from the ground vibrational level ($v = 0$) to the third excited vibrational level ($v = 3$). The second laser, supplying a UV photon of 2650Å, then excites the system to the repulsive electronic state $A^1\Pi$, on which the molecule can dissociate. [In the experiment on HCl reported by Letokhov (1973), the second photon is actually generated by the 4-th harmonic of the first

laser, which is a dye laser pumped by a Nd:glass Q-switched laser.] The photodissociation cross section is observed to be $\sim 10^{-19}$ cm^2. Other examples of photodissociation based on this process include the isotope separation of ^{15}N from $^{15}NH_3/^{14}NH_3$, B from BCl_3/O_2, ^{50}Ti from $TiCl_4$, and D,T, ^{16}O, ^{18}O from either H_2O/CO or $H_2O/CO + C_2H_4$.

The following process (Yeung and Moore, 1972), provides a good example of laser-induced predissociation:

$$H_2CO + \hbar\omega(3472\text{Å}) \rightarrow H_2CO^* \rightarrow H_2 + CO.$$

In this example, only one laser is required. The 3472Å photon excites the system from the ground vibrational level of the ground singlet electronic state to an excited vibrational level of the excited singlet electronic state. Dissociation then occurs through crossing of the latter electronic state with a repulsive electronic state. By selectively choosing laser frequencies to excite isotopically distinct vibrational levels, the isotpic species ^{13}CO, ^{14}CO and $C^{18}O$ can be separated. Also H_2CO can be separated from H_2CO/D_2CO mixtures.

In many instances, LIS can be effected by employing a scavenger which reacts preferentially with a species in its excited state. An intense laser can then be used to selectively excite an isotopic species. The unwanted isotopic species would simply absorb no photons and hence would not react with the scavenger. A prototype of this process is (Zare, 1977):

$$I^{37}Cl + \hbar\omega(6050\text{Å}) \rightarrow I^{37}Cl^*$$

$$I^{37}Cl^* + C_6H_5Br \rightarrow I + Br + {}^{37}ClC_6H_5.$$

The bromobenzene (C_6H_5Br) is acting as the scavenger; it only reacts with ICl^* (excited electronic state). The $I^{35}Cl$ in the sample will not absorb any 6050Å photons and remains in the ground electronic state. Hence it is incapable of reacting with the C_6H_5Br.

B. Multiphoton Processes

1. Atomic Systems

We first discuss multiphoton processes in atomic systems, where electronic transitions in atoms involve the simultaneous absorption or emission of more than one photon. By using sufficiently high-energy photon fluxes, a variety of nonlinear electronic transitions may be observed (Eberly and Lambropoulos, 1978). Some of the important examples are: (i) multiphoton ionization (simultaneous absorption of more than one photon leading to the emission of an electron), (ii) electronic Raman scattering, elastic/inelastic photon scattering and resonance scattering (absorption of photons with frequency ω followed by the emission of photons with frequency ω'), (iii) third harmonic generation (absorption of three photons of equal frequnecy ω with the emission of one photon of frequency 3ω) and (iv) infrared up-conversion (absorption of three photons of different frequencies with the emission of one photon of the sum frequency, 3ω).

A number of theoretical and experimental investigations on multiphoton processes in atomic systems have been reported in

the literature (Eberly et al., 1979). Here we shall only focus on the multiphoton transition probability and the ionization probability of a multilevel atomic system.

It has been known that the multiphoton transition probability of an atomic system can be greatly increased via intermediate states with frequency nearly resonant with the driving radiation field. As long as the pumping rate does not exceed the binding energy of the electron, or for laser powers not higher than 10^{16} W/cm^2, perturbation theory is usually adequate for a theoretical description. Time-dependent first-order perturbation theory gives the probability of finding an electron in the upper state of a two-level atom as (Sargent et al., 1974)

$$P_{0\to 1}(t) = \frac{|V|^2}{\Delta^2+(\gamma/2)^2}\left[1 + e^{-\gamma t} - 2\cos(\Delta t)e^{-\gamma t/2}\right], \quad (1)$$

where V is the pumping rate (proportional to the electric field of the radiation), and Δ and γ are the detuning and the width of the upper level, respectively. We note that the above functional form for a single-photon transition can also be used to describe a two-photon transition by defining the two-photon detuning $\Delta = \omega_f - 2\omega$ and $\gamma = \gamma_f$, where ω_f and γ_f are the frequency and width of the final state and ω is the field frequency. In this two-photon process, the pumping rate V is now replaced by

$$|V^{(2)}| = \left|\sum_j \frac{V_{fj}\, V_{jg}}{i\Delta_j + \gamma_j/2}\right| \quad (2)$$

where j is the intermediate state with frequency ω_j and width γ_j, and $\Delta_j = \omega_j - \omega$ is the detuning.

The above approach is satisfactory if no intermediate state is situated at resonance. This process, without an intermediate resonance, is called "coherent", and in general, for a system consisting of a set of intermediate states, we can have both coherent and incoherent excitations.

The transient behavior of a two-photon process, has been experimentally observed using Doppler-free excitation of a cell of sodium atoms (Bassini et al., 1977). By using Eq. (1), we generate the absorption profiles shown in Fig. 3: these curves qualitatively show the experimentally observed absorption transients in sodium for various two-photon detunings (Lin and George, 1981a).

A generalization of the two-photon excitation gives us the ionization probability for an N-photon process with nearly-resonant intermediate states (Stenholm, 1979),

$$P_{ion} = \beta I^N, \tag{3}$$

where β is a constant of proportionality and I is the intensity of the laser field. The type of behavior characterized by the order N has been experimentally observed for many atoms with N ranging from 5 to about 20 (Delone, 1975). However, when an intermediate resonance occurs, there are deviations from the simple law of Eq. (3). Fig. 4 shows the intensity dependence of three-photon ionization in cesium at the ruby laser frequency (Georges and Lambropoulos, 1977). It is seen that the plot of

log P_{ion} versus log I departs from the straight line of slope 3 found in nonresonant processes [Eq. (3)]. This behavior has been observed in a number of experiments and can be understood in terms of the strong radiative interaction with nearly-resonant intermediate states which are coupled to the continuum (ionization) staces and shifted and broadened due to multilevel effects. We note that the field-induced Stark shift and level broadening for an atomic system are similar to the frequency shift and damping effect in a gas/surface system where many-body effects can be treated by the Wigner-Weisskopf approximation (Louisell, 1973).

2. Molecular Systems

In molecular systems, although visible and ultraviolet photons have the most pronounced effects on the chemical properties of molecules, much attention has been paid to infrared photochemistry since the first report of laser-isotope separation (Ambartzumian et al., 1974). A considerable amount of theoretical and experimental research has resulted from the suggestion that multiphoton excitation (MPE) could be a novel method for vibrational-mode control of molecular decomposition (Schulz et al., 1979; Letokhov, 1980; Lee and Shen, 1980). Sulfur hexafluoride (SF_6) was one of the first molecules to be dissociated by a high-power CO_2 laser. The pressure dependence of isotopic selectivity in the multiphoton decomposition (MPD) of SF_6 (Ambartzumian et al., 1974, 1975; Lyman et al., 1975) suggests that the dissociation takes place under collisionless conditions,

as further confirmed by molecular beam experiments (Kompa, 1976).

A well-accepted qualitative model for MPD of SF_6 has provided a general picture where the molecular energy levels are divided into three regions: (I) the discrete region characterized by coherent excitation, where the ν_3 (active) mode absorbs 3 to 6 photons and the anharmonicity of the vibrational potential is nearly compensated for by allowed rotational transition; (II) the quasi-continuum region where the level density is very high and incoherent excitation is essential; and (III) the true continuum region. Region (I) processes are responsible for isotopic selectivity, coherent effects (multiphoton resonance, photon echoes, coherent wave propagation, etc.) and the intensity dependence of MPE with high selectivity. For the excitation processes in regions (II) and (III) it has been shown experimentally that high laser fluence (energy), not high laser power (intensity), is necessary for driving the molecule through the quasi-continuum and is the important parameter for determining the dissociation yield (Grant et al., 1978).

The phenomenon of infrared MPE and MPD seems well understood qualitatively. However, quantitative understanding hinges on the following fundamental questions:

(i) What are the roles of coherent and incoherent absorption processes in MPE and MPD? What is the magnitude of the absorption cross section and how does it change with molecular parameters (dipole moment, level width, anharmonic potential, etc.), the intensity, fluence, frequency and degree of coherence of the laser radiation?

(ii) How selective is the particular MPD? How fast does the energy in the pumped active mode randomize with the other degrees of freedom via inter- and intramolecular energy relaxations?

(iii) What is the energy distribution pattern of the absorbed photons among the vibration-rotation states of the molecule?

(iv) What is the dynamics of the dissociation event and what are the parameters that determine the rate of unimolecular decomposition?

(v) How can selectivity in laser chemistry be achieved by novel methods such as multistep excitations?

In order to answer the above questions either qualitatively or semi-quantitatively, we shall first discuss some recent theoretical approaches using classical and quantum models, and, subsequently, the selectivity aspects of laser chemistry.

a. Classical Models

Due to the high density of states at most energies in a typical molecule, rigorous quantum mechanical treatments of multiphoton processes are presently impractical. Classical studies, however, do not suffer from such a difficulty although many quantum effects cannot always be successfully incorporated (Bloembergen, 1975; Cotter et al., 1976; Walker and Preston, 1977; Steverding et al., 1977, 1978; Lin, 1979).

Consider a polyatomic molecule subject to an intense infrared radiation field. By singling out the active vibrational mode (e.g., the ν_3 mode for SF_6 molecule) as an anharmonic

classical oscillator and the remaining modes as the heat bath, we may describe the dynamics of the system by the following nonlinear equation of motion (Lin, 1979):

$$\ddot{Q} + 2\gamma\dot{Q} + \omega_o^2 Q + \alpha Q^2 + \beta Q^3 = f(t)/m, \tag{4}$$

where Q is the normal coordinate of the active mode (with fundamental frequency ω_o), α and β are the anharmonic coefficients, m is the reduced mass and f(t) is the driving force. We note that the above single-body equation may be rigorously derived from a many-body system (Lin and George, 1981a). By the harmonic balance method (Minorsky, 1962), Eq. (4) can be linearized by introducing an amplitude-dependent effective frequency (Lin, 1979). The solution of the linearized equation gives us the power absorption of the anharmonic oscillator. For this simple system with a constant damping factor γ, we obtain the power absorption and also the absorption cross section as a Lorentzian. However, for a more realistic system, the damping factor could be time dependent and the phase of the oscillator could also relax due to incoherent processes. For this purpose, instead of Eq. (4), we now consider the generalized Langevin equation (GLE) (Lin and George, 1980a)

$$\ddot{Q} + \int_o^t \beta(t-t')\,\dot{Q}(t')dt' + \omega_{eff}^2 \int_o^t M(t-t')\dot{Q}(t')dt' = [f(t) + R(t)]/m. \tag{5}$$

Here we have introduced the damping kernel β and the dephasing kernel M to describe the interaction dynamics between the active

mode and the bath modes. $f(t)$ and $R(t)$ are the laser driving force and the bath-induced random force, respectively. ω_{eff} is the effective frequency of the active mode related to the fundamental frequency ω_o, the anharmonicity K^* and the bath-induced frequency shift $\delta\omega$ by

$$\omega_{eff} = \omega_o - K^* A^2 - \delta\omega, \tag{6}$$

where A is the steady-state amplitude of the oscillator and is proportional to the applied laser intensity. The above GLE enables us to study the dynamics of classical multiphoton absorption via T_1(energy) and T_2(phase) relaxations, which are governed by $\beta(t)$ and $M(t)$ respectively. For given forms of the memory functions $\beta(t)$ and $M(t)$, we are able to calculate the velocity autocorrelation function, which in turn gives us the (time- and ensemble-) averaged energy absorption rate. For the case of Markovian processes and an exponentially decaying phase, we obtain

$$\overline{\left\langle \frac{dE}{dt} \right\rangle} = (qE_o)^2 P(T_o) [\gamma_2 A + \omega B]/[A^2 B], \tag{7}$$

$$P(T_o) = (2\hbar\omega)^{-1} (kT_o/m) [1-\exp(-\hbar\omega/kT_c)], \tag{8}$$

$$A = \omega_{eff}^2 - \omega^2 + \gamma_1\gamma_2, \tag{9}$$

$$B = \omega(\gamma_1 + \gamma_2), \tag{10}$$

where q and T_o are the classical charge and the initial temperature of the molecule, respectively; E_o is the electric field of

the laser radiation and γ_1 and γ_2 are the energy damping factor and the dephasing factor, respectively. We note that the absorption cross section (or the lineshape), which is proportional to the energy absorption rate, which is characterized by the overall broadening $(\gamma_1 + \gamma_2)$ and detuning $(\omega_{eff} - \omega)$, and is in general asymmetric due to the dephasing term $\gamma_2 A$. For the case of incoherent processes $\gamma_2 >> \gamma_1$, and the line broadening is dominated by the T_2 dephasing. On the other hand, for the coherent processes $\gamma_1 >> \gamma_2$, and the lineshape reduces to the symmetric Lorentzian governed by the simple equation of motion Eq. (4).

In addition to the above phenomenological models, a classical trajectory calculation of MPE has been recently made for SF_6 (Poppe, 1980). The results show that the energy transfer and dissociation rate depend on laser fluence (intensity × time), and the intramolecular energy relaxation rate is estimated to be on the order of a picosecond.

Another classical treatment of MPE and MPD for a system of two nonlinearly coupled oscillators was studied by means of Krylov-Bogoliubov-Mitropolsky theory (Ramaswamy et al., 1980). The results show two regions of behavior for the exchange of energy between the system and the laser field: (I) the regular region with well-defined frequencies and (II) the erratic region. Motion in the latter region leads to dissociation of the pumped molecule.

2. Quantum Models

Two distinctly different approaches for building simplified quantum mechanical models of MPE and MPD have been used. In the first approach (referred to as the heat-bath model), attention is focused on the active vibrational mode. The second approach treats all vibrational modes on an equal footing and deals with transitions between true molecular eigenstates, induced by the laser field. We first discuss the heat-bath model. The total system may be described by the Hamiltonian

$$H(t) = H_A + H_B + H_{AB} + H_{AF}, \tag{11}$$

where H_A and H_B represent the unperturbed Hamiltonians of the active and both modes, respectively, H_{AB} represents the anharmonic coupling between the active and the bath modes and H_{AF} represents the interaction between the active mode and the laser field.

In the Heisenberg-Markovian picture (Louisell, 1974), the above Hamiltonian, expressed in a second-quantization form, has been used to calculate the average excitation of the active mode for the case of linear coupling in H_{AB} (Narducci et al., 1977) and high-order coupling (Gan et al., 1978; Lin and George, 1981b). The key feature of multiphoton absorption in the heat-bath approach may be clearly described by the equation,

$$\frac{dn_A}{dt} = \sigma I - \gamma(n_A - \bar{n}), \tag{12}$$

where n_A and $\bar{n}$ are the average excitations of the active mode and the heat-bath modes, respectively. I is the laser intensity, γ is the damping factor describing the T_1(energy) relaxation of the pumped mode and σ is the absorption cross section. We note that Eq. (12) is based on energy conservation and can be derived rigorously from a microscopic Hamiltonian (Lin, 1980). The steady-state excitation may be easily found by $n_A^{s.s.} = \sigma I/\gamma + \bar{n}$ which gives us $n_A^{s.s.} \propto I$ for harmonic or low excitations (σ independent of $n_A^{s.s.}$) and $n_A^{s.s.} \propto I^{\alpha}$, with $\alpha < 1$ for anharmonic or high excitations (σ is excitation dependent). Furthermore, the average number of photons absorbed by the molecule (active plus bath modes) is given by the time integral of the pumping rate σI, which yields the fluence(ϕ)-dependent form $\langle n_m \rangle \propto \phi^{\beta}$, with $\beta = 1$ and 1/3 for the harmonic and highly anharmonic cases, respectively.

We now discuss the second quantum approach which treats all vibrational modes on an equal footing, with the eigenstates of the system being mixtures of all the normal modes. Due to the high density of vibrational states at high excitation energy, the molecule can easily absorb more photons through resonant incoherent transitions between so called quasi-continuum levels, where rate equations have been widely used for collisionless MPD (Quack, 1978; Thiele et al., 1980; Grant et al., 1978; Fuss, 1979;

Barker, 1980; Baldwin and Barker, 1981) and collisional MPD (Troe, 1977; Tardy and Rabinovitch, 1977; Stone et al., 1980).

For multiphoton excitation in the quasi-continuum region, the Fermi Golden Rule is valid and the full Schrödinger equation reduces to a set of incoherent rate (master) equations. For the collision-free condition (low pressure), the rate equations for the energy population are:

$$\frac{dP_n}{dt} = W^a_{n-1}P_{n-1} + W^e_n P_{n+1} - (W^a_n + W^e_{n-1})P_n - k_n P_n, \qquad (13)$$

where P_n is the population in the n-th level (n photons absorbed). W^a_n (W^e_n) is the transition rate constant for absorption (emission) from level n to n+1 (n+1 to n) and is related to the absorption cross section (σ_n) and frequency of the field (with intensity I) by $W^a_n = \sigma_n I/\hbar\omega$ and $W^e_n/W^a_n = g_n/g_{n+1}$, where g_n is the molecular density of states at energy $n\hbar\omega$. k_n, the unimolecular decomposition rate constant, can be calculated by RRKM theory (Forst, 1973) or quantum RRK theory (Shulz and Yablonovitch, 1978). From Eq. (13) we realize that collisionless MPE and MPD are characterized by the laser intensity and frequency, the absorption cross section, the density (or degeneracy) of states and the unimolecular reaction constant. During the past several years, the rate equations describing MPD have been studied by different approaches, such as a thermal model for Boltzmann-type energy populations (Black et al., 1979), diffusion model for continuum populations (Fuss, 1979), exact stochastic model (Baldwin and Barker, 1981),

the model of restricted intramolecular relaxation (Stone and Goodman, 1979) and the random coupling model (Carmeli and Jortner, 1980).

In the thermal model, the population P_n is given by a Boltzmann function

$$P_n = A \exp(n\hbar\omega/kT_{eff}). \tag{14}$$

A is the preexponential factor and T_{eff} is the effective vibrational temperature given by the energy conservation equation

$$S\bar{n} = \langle n\rangle\hbar\omega, \tag{15}$$

$$\bar{n} = [\exp(\hbar\omega_o/kT_{eff}) - 1]^{-1}, \tag{16}$$

Here ω_o is the mean frequency of the molecule with S vibrational modes and average number $\langle n\rangle$ of absorbed photons. It is noted that for multiphoton processes with $kT_{eff} >> h\omega_o$, Eq. (15) reduces to the simple form $kT_{eff} \simeq \langle n\rangle h\omega/S$. The corresponding dissociation probability P_d can be easily found by Eq. (14) based on the threshold number of photons for dissociation n^*,

$$P_d = \sum_{n=n^*}^{\infty} P_n \propto \exp(-Sn^*/\langle n\rangle), \tag{17}$$

which is the usual Arrhenius form.

Depending on the forms of the transition rate constants, W_n^a and W_n^e, the solution of the rate equation gives us different

populations and the corresponding dissociation probabilities. Some important populations and their corresponding dissociation probabilities are shown in Fig. 5 (Lin and George, 1979b; George et al., 1980).

C. Discussion

(i) Selectivity in Laser Photochemistry

Selectivity is characterized not only by the coherent properties of the laser field but also by the molecular properties of the excited system. Therefore, the types of selectivity in infrared multiphoton excitations can be classified according to the relation between the various relaxation times of the excited system and the energy pumping rate of the laser field (Letokhov, 1980). Let us first define R^{intra} and R^{inter} as the intra- and intermolecular vibrational energy transfer rates, respectively, R^{V-T} as the relaxation rate for molecular vibration-translation coupling, i.e., $(R^{V-T})^{-1}$ is the time for complete thermal equilibrium to be reached in the molecular mixture, and W_{exc} as the rate of vibrational multiphoton excitation of the molecule. We can distinguish four different types of selectivity depending on the relative magnitudes of the relaxation rates and the laser excitation rate (note that the relaxation rates R^{inter} and R^{V-T} are pressure dependent, although for low pressures we shall expect that $R^{V-T} << R^{inter} << R^{intra}$):

(I) Mode (bond)-selective excitation ($W_{exc} >> R^{intra}$).

A certain mode or a functional group of a polyatomic molecule is in a nonequilibrium state which has a higher vibrational temperature T_{eff} [defined by Eq. (15)] as compared with the remaining modes or functional groups. This is the situation of a long lifetime or high pumping rate.

(II) Molecular-selective excitations ($R^{intra} >> W_{exc} >> R^{inter}$). In this case the absorbed photon energy is rapidly randomized within the excited molecule in which the local vibrational temperature is higher than the overall translational temperature of the mixture of different molecules.

(III) Vibrational-selective excitation ($R^{inter} >> W_{exc} >> R^{V-T}$). In this more moderate condition, vibrational equilibrium among all the mixed molecules is reached, but there is still no overall thermal relaxation. This situation prevails for low pressures, where vibration-translation relaxation rates are lower than vibration-vibration relaxation rates.

(IV) Nonselective thermal excitation ($R^{V-T} >> W_{exc}$). This is the situation of thermal excitation of all the molecules in a mixture by a low-power CW laser. This field of infrared thermal chemistry is of interest for a heterogeneous system (e.g., species adsorbed on a solid surface), where the laser radiation is used to excite the adsorbed gas molecules without significantly heating up the solid surface (assuming the phonon coupling to be small). We shall discuss this type of excitation in Section III.B.2.

The attraction of infrared laser chemistry is that if the photon energy can be deposited and maintained in a specific

vibrational mode (or functional group), a selective reaction involving that mode (functional group) may be induced. Therefore, one of the critical questions concerning MPD processes is whether the photon energy remains localized in the pumped mode (or molecule) long enough to result in a mode selective (or molecule-selective) reaction. Most theoretical models of MPD assume that intramolecular vibrational relaxation (IVR) is very fast (on the order of a picosecond), and statistical approaches such as RRKM theory have been applied successfully to a number of experimental results (Black et al., 1979; Sudbo et al., 1979). Recently, however, several experiments examining product branches ratios in relatively complex molecules, e.g., cyclopropane, have shown that the laser selectivity could not be explained by the statistical theory (Hall and Kaldor, 1979). The evidence suggests that the laser-induced reactions could result from a nonergodic or partially mode-selective excitation. Several research groups have also examined the bond localization character of large molecules, e.g., benzene, both experimentally and theoretically (Zewail, 1980; Bray and Berry, 1979; Heller and Mukamel, 1979; Thiele et al., 1980). This nonstatistical behavior is explained by a local mode model in which the total system is divided into two groups of vibrational modes. Within each group, the vibrational modes are strongly coupled and the photon energy quickly randomized. Between groups, however, the coupling is considerably weaker, and intergroup randomization rates are therefore appreciably slower by the concept of the energy-gap law (Nitzan et al., 1975). Another theory called the "restricted IVR model" has been recently

proposed for the possibility of laser-selective photochemistry (Thiele et al., 1980).

(ii) Multistep Excitations

It has been experimentally shown that the dissociation yield of a molecule may be greatly enhanced via a two-step excitation$^{(IR + UV)}$ combining a single-step IR process with a single-step UV process. Strictly speaking this is not a multiphoton process, but is rather a sum of two uncorrelated single-photon events as mentioned in Section II.A. However, there is the possibility in this situation of multiphoton excitation, particularly from the IR laser. One could also replace the UV laser with several IR lasers, e.g., two, to achieve a multistep (three-frequency) excitation. Using a set of three phased pulses with frequencies resonant to the energy separations of three anharmonic level pairs and with pulse durations equal to different integral multiples (n) of π, efficient photon energy absorption can be achieved. In this process, the successive lasers interact with the molecule when the population is completely inverted by the first, i.e., at the moment of time $t = \tau$, such that $\Omega\tau = (2n+1)\pi$, where Ω is the Rabi frequency (Oraevski et al., 1976).

A classical treatment of the dissociation of HF by two differnet IR lasers has shown (not surprisingly) that lower laser power densities of each laser are required for molecular dissociation than for a corresponding single-laser process (Stine and

Noid, 1979). Recently, a quantum model of two-laser excitation of SF_6 has also suggested the advantage of multistep excitation (Narducci and Yuan, 1980).

III. Molecular Interactions and Reaction Dynamics

A. Gas-phase Processes.

The main feature of laser-induced dynamical processes is that laser photons do not have to be in resonance with the asymptotic separations in energy levels of the collision species (DeVries et al., 1980). This means that light absorption and collisional energy transfer do not take place as independent events. There are two viewpoints of looking at the situation: atomic and molecular. For simplicity let us consider atom-atom collisions A + B. The atomic description makes use of asymptotic atomic energy levels of the A + B system. For example, one can refer to the Na(3p) + Na(5s) energy level of the Na-Na system in the separated-atom limit. A photon slightly detuned from resonance (with respect to the atomic energy levels) will still be absorbed, the difference in energy being made up for by the collision. In the molecular picture, however, we can still speak of a resonance absorption process, only that in this case the electronic energy levels are changing as a function of internuclear distance (as represented by interatomic potential energy curves) and the absorption takes place at some finite internuclear separation where the resonance condition is fulfilled. The two

points of view are illustrated in Fig. 6. In the second picture the inseparability between radiative interaction and collision dynamics is brought out much more succinctly.

Theoretically one can exploit this inseparability to introduce a mode of description of laser-influenced collision processes known as the electronic-field representation (George et al., 1977). This representation is based on the idea of "dressing" molecular quantum states with photon quantum states. The resulting "dressed" states allow description of collisional and radiative interactionson the same footing and reveals clearly the altered dynamics of a collision system due to the presence of the radiation. The simplest way to introduce the electronic-field representation is as follows. We begin with a set of potential curves corresponding to different electronic energy levels of the collision system. Suppose an intense coherent laser of frequency ω is applied. All the curves are then shifted by an amount $h\omega$. The set of shifted and unshifted curves may cross each other at several points. At every crossing between a shifted and unshifted curve, radiative interaction is effective and the curves "couple" with each other to generate an avoided crossing. These avoided crossings change the shapes of the curves and thus effectively change the dynamics of the system. The radiatively altered curves are called electronic-field curves and the quantum mechanical representation that they generate is known as the electronic-field representation.

The use of these curves can be illustrated by Figs. 7 and 8. Fig. 7 represents a nonreactive and Fig. 8 a reactive

situation. The (a) portions of both figures represent the field-free and field-shifted potential curves with real crossings whereas the (b) portions represent the electronic-field curves with avoided crossings. The relevant curves for the description of dynamics in Figure 7(a) are E_1 and E_2 which correspond asymptotically to $W_1 + \hbar\omega$ and W_2, respectively. In this example, the barrier in the field-free curve W_1 has been turned into a shallow valley (on E_1), and the valley in the field-free curve W_2 has been turned into a barrier (on E_2), thus showing clearly the effect of the radiation field in altering the dynamics of the system. In Figure 8(a) W represents a reactive curve exothermic with respect to reaction (reaction coordinate running from right to left), while W_2 and W_3 both exhibit steep reaction barriers. The presence of a strong field changes the situation altogether [Fig. 8(b)]. A reaction starting on the surface $W_1 + \hbar\omega$ could now be diminished while one starting on surface W_2 would actually become exothermic. A reaction staring on W_3 could also be enhanced. This example again illustrates the significant effects on dynamics due to the presence of the field.

We shall now indicate some actual systems illustrating collisional energy transfer in the presence of intense laser fields. First we mention the pioneering experiment (Falcone et al., 1977):

$$Sr^*(5p,\ ^1P_o) + Ca(4s^2,\ ^1S) + \hbar\omega(4976.8\text{Å}) \rightarrow Sr(5s^2,\ ^1S) + Ca^*(4p^2,\ ^1S).$$

This process can be described as an example of "cooperative collisional and optical pumping". In the atomic picture, the excitation of the $Sr^*(5p, {}^1P_o)$ is transferred to $Ca^*(4p, {}^1P_o)$ by collision and the photon then pumps the Ca to $Ca^*(4p^2, {}^1S)$. Pure optical pumping would not have been able to excite $Ca(4s^2, {}^1S)$ to $Ca^*(4p^2, {}^1S)$ because of unchanged parity between the initial and final states. In the molecular picture one would use potential surfaces corresponding asymptotically to the energies $Sr^*(5p, {}^1P_o) + Ca(4s^2, {}^1S) + \hbar\omega$ and $Sr(5s^2, {}^1S) + Ca^*(4p^2, {}^1S)$. Another example of laser induced collisional energy transfer is given by (Cahuzac and Toschek, 1978):

$$Eu({}^8P_J) + Sr({}^1S_o) + \hbar\omega_2(\lambda_2 \simeq 658nm)$$

$$\rightarrow \quad Eu({}^8S_{7/2}) + Sr({}^1D_2)$$

where J = 5/2, 7/2 or 9/2. This process can be described analogonsly to the last example.

An example of laser-induced reaction is given by (Hering et al., 1980):

$$K(4^2S) + HgBr_2, + \hbar\omega \ (595nm)$$

$$\rightarrow KBr + HgBr^* \ (B\ ^2\Sigma) \rightarrow \ KBr + HgBr(X^2\Sigma^+) + \hbar\omega_2(500nm).$$

No single-photon absorptions are known for $\lambda \sim 590nm$ for either reagents or products of this system. Hence resonance for $\hbar\omega$ can only be fulfilled for some transition state (existing only for finite reaction coordinates) (Hering et al., 1980). The fact that

$HgBr^*(B\ ^2\Sigma)$ is formed is inferred from the fluorescence of 500nm to the ground state $HgBr(X^2\ \Sigma^+)$. Another example is the reaction (Wilcomb and Burnham, 1981)

$$Xe + Cl_2 + \hbar\omega(193.3nm) \rightarrow XeCl^*(B,C) + Cl$$

which does not proceed in the absence of the ArF laser.

Two dynamical processes resembling laser-induced collisional energy transfer (insofar as altered dynamics as a result of radiative interaction is concerned) are laser-induced Penning and associative ionization. The laser again does not have to come in resonance with asymptotic energy levels. It interacts with the collision system mainly at finite internuclear separations. The ionization usually takes place via cooperative optical and collisional excitation to some excited electronic state whose potential curve is either embedded in the ionization continuum (generated by the continuous range of free electronic energies) (Bellum et al., 1978; Bellum and George, 1979) or crosses the ionization threshold curve at some finite nuclear separation. Both kinds of ionization (Penning and associative) have been reported recently in the study of the Na-Na system (Polak-Dingels et al., 1980):

$$Na + Na \xrightarrow{\hbar\omega} Na_2^+ + e \quad \text{(associative)}$$

$$Na + Na \xrightarrow{\hbar\omega} Na^+ + Na + e \quad \text{(Penning)}.$$

B. Condensed Phases

1. Liquids

Applications of lasers in the chemistry of pure liquids or solutions have exploited two characteristics of laser radiations: (i) monochromaticity and (ii) ultrashort high-intensity pulses; the former involves excitation of specific vibrational modes, while the latter is used in ultrafast, relatively nonspecific heating of the sample in the so-called laser temperature jump relaxation spectroscopy. The use of picosecond pulses of laser radiation allows a study of ultrafast (psec. time scale) processes in liquids such as orientational or rotational relaxation, electron transfer, vibrational dephasing or energy transfer, electronic energy transfer, formation of charge-transfer complexes, photo dissociation, recombination of ions to form molecules in a "cage" of solvent molecules and a variety of other ultrashort transient phenomena.

Laser light scattering experiments can be designed to measure either the polarized or the depolarized component of the output signal. Since the latter is often many orders of magnitude smaller than the former, intense laser sources are necessary for meaningful detection of the depolarized light scattering. A large amount of valuable information, especially about dynamical many-body effects in liquids, has been obtained from this new spectroscopy.

Liquid-phase laser chemistry can be divided into three

categories, albeit somewhat arbitrarily since there are substantial overlaps between them: (a) light scattering studies (polarized or depolarized), (b) laser-induced chemical reactions, and (c) time-resolved studies using ultrashort laser pulses.

a. Laser Light Scattering

Thermal fluctuations of the dielectric constant of a medium cause an incident polarized beam of laser light to scatter. The total scattering intensity can be thought of as a superposition of scattering from individual molecules, and the static and dynamic correlations between these are reflected in the output signal. In addition to the large component with polarization similar to that of the incident light, a depolarized component due to intrinsic (or collision-induced) anisotropies in the polarizabilities of the molecules is present in the scattered light. The two provide information about different types of relaxation processes in the system (Bauer et al., 1976; Berne and Pecora 1976).

Experimental techniques in this field differentiate between processes faster than 10^{-6} sec., and those slower than 10^{-6}sec. (Berne and Pecora, 1974; Fleury and Boon, 1973). Filter methods (Benedek, 1968) involving frequency-scanning by a grating monochromator (10^{10} - 10^{14} Hz) or a Fabrey-Perot interferometer (10^{6} - 10^{11} Hz) are used for the former case, and provide the autocorrelation function $\langle E_s^*(0)\ E_s(t)\rangle$, where E_s is the amplitude of the electric field of the scattered electromagnetic radiation. In contrast, processes slower than 10^{-6} sec. are investigated

by techniques involving optical beats (Cummins, 1971) ("optical mixing"): the heterodyne method gives $Re\langle E_s^*(0)\ E_s(t)\rangle$ while the homodyne method gives $\langle|E_s(0)|^2 \cdot |E_s(t)|^2\rangle$. We discuss a few applications below.

Diffusion of Small Macromolecules (Ford, 1972). Time scales for these processes being 10^{-3} - 10^{-1} sec, optical mixing methods are applicable. Polarized scattering studies provide information on the dimensions and molecular weights of the macromolecules, the concentration dependence of diffusion coefficients and aggregation effects. A striking example of the latter is a study of the onset of aggregation of hemoglobin S molecules (Wilson et al., 1971). The high molecular weight of an aggregate results in a larger contribution to the time correlation function (because of its smaller diffusion coefficient relative to that of a monomer). This results in a high sensitivity of light scattering to small amounts of aggregation. Exploitation of this sensitivity made possible the detection of aggregation of hemoglobin S molecules.

Orientational Relaxation of Small Molecules (Fujime, 1972). Two distinct situations exist in solutions of small molecules. For the case where correlations between different molecules are negligible, one obtains single-molecule relaxation times. For strongly correlated molecules, however, collective orientational relaxation becomes important, and it is necessary to separate the degrees of freedom into slowly and quickly relaxing ones. A statistical mechanical formalism due to Mori, (Mori, 1965a,b) based on a calculation of the temporal behaviour of the slowly-relaxing modes then provides an interpretation of both the static and the dynamic correlations in the fluid. These are contained

in the linewidths and intensities of the Lorentzian curves, one for each different type of anisotropic molecule present.

CW HeNe, Ar^+ and Kr^+ lasers are used, and the filter method is necessary because of time-scales $\sim 10^8 - 10^{11}$ Hz. Some general qualitative features have emerged from studies involving depolarized light scattering (Bauer et al., 1976). Thus, for pure aromatic molecules (high concentration limit), orientational relaxation behavior is in qualitative agreement with the Stokes-Einstein Theory, viz. $\tau \propto \eta/T$, η being the viscosity and T the temperature. For dilute solutions, however, $\tau = C\eta + \tau_o$ with substantial quantitative deviations of C from the Stokes-Einstein theory.

Results of similar studies have provided information on the influence of solvent hydrogen bonding on reorientation (Alms et al., 1973a,b) as well as tests of various assumptions (Einstein, 1956; Adler et al., 1970; Hu and Zwanzig, 1974; Youngren and Acrivos, 1975), e.g., "stick" or "slip" boundary conditions, made in connection with the viscosity dependence of reorientation times in hydrodynamical theories of fluid motion.

Particularly clear and detailed interpretation of the rotational dynamics is possible for systems where the collisional part of the correlational function is known to be small (Bruining and Clarke, 1975; Schoen et al., 1975), for example, liquid CO, O_2 and N_2. The spectra of these molecules were found to be roughly Gaussian. Furthermore, the results for N_2 and CO are consistent with an average 50° rotation between collisions.

Electrophoretic Light Scattering (Ware, 1974). For solutions

of macroions, electrophoresis and the heterodyne method are combined to provide a powerful technique for measuring mobilities, diffusion coefficients and relative concentrations in ionic mixtures. The very high resolution and speed (relative to conventional electrophoresis) as well as the ability to use very low concentrations make electrophoretic light scattering a very attractive technique for chemical kinetics. Systems to which this technique has been applied include (Bauer et al., 1976; Ware, 1974; Bennett and Uzgiris, 1973; Uzgiris and Kaplan, 1974; Uzgiris, 1974) polystyrene latex spheres, the bacterium staphyloccus epidermis, human erythrocytes and bovine serum albumin monomers and dimers. Intensity Fluctuation Spectroscopy (Schaefer and Berne, 1972; Schaefer, 1974). This technique applies particularly to very dilute solutions of large (micron size) molecules, which move independently. Two widely separated time scales are involved in the fluctuations of the system, τ_N related to the volume defined by the intersection of the incident and detected beams, and τ_q related to the scattering length q. These are referred to as the number and interference fluctuation times, respectively. Variations of τ_N provide an elegant method for studying a variety of processes which involve a net flux of particles.

b. Laser-Induced Chemical Reactions.

A prominent technique for stimulating chemical reactions with lasers utilizes ultrashort pulses ($\sim$1 psec) of intense radiation in temperature jump spectroscopy (Flynn and Sutin, 1974).

This method belongs to the class of line-broadening or relaxation methods, the latter involving a very fast perturbation of the system away from equilibrium. The temperature jump method is very popular because it requires only that the reaction being studied have a non-zero enthalpy change $\Delta H°$, as opposed to, say, ultrasound absorption, which requires a finite volume change, or dielectric relaxation which requires a change in the effective electric moment. With a laser providing the temperature jump, very fast heating times ($\sim$1 psec) can be realized and very small samples can be used because of the focussing capabilities of laser beams.

Nd:glass and ruby lasers have sufficient power density ($\sim 10^8$ W/cm^2) for effective temperature jumps in many solvents other than water. Dyes are often used in aqueous solutions to overcome this problem. For systems of biological interest, however, techniques which exploit the stimulated Raman effect to red-shift the output of a Nd:glass or ruby laser, are available to provide wavelengths absorbed by water.

The technique is most effective for studying reactions which are first order in the forward and/or backward direction. Typical applications are intersystem crossings in octahedral transition-metal complexes (Beattie et al., 1973) and the tri-iodide ionic equilibrium (Turner et al., 1972):

$$I_2 + I^- \rightleftharpoons I_3^-$$

The Raman laser temperature jump study of this reaction

(in aqueous solution) provided an understanding of the intermediate steps, including a water exchange rate, and numerical values of the rate constants.

Instead of inducing reactions via a temperature jump in the solvent, direct absorption of the laser energy by the solute molecules can be utilized to study mecahnisms and reaction kinetics. A simple but important application of the method is the photoionization of water (Goodall and Greenhow, 1971). In a recent study of the wavelength and temperature dependence of the quantum yield for the laser-induced ionization, it was shown that a single photon is sufficient, and that the quantum yield increases dramatically with photon energy (Goodall et al., 1979). The study also provided an understanding of the relative importance of decomposition and relaxation channels in the kinetic process.

In addition to pulsed lasers, CW lasers have also been used in the study of certain electronic excitations in solution. Examples include production of O_2 in the singlet state (Matheson and Lee, 1970), trans-cis isomerization of indigo dyes and subsequent cis-trans conversions (Giuliano et al., 1968) and the study of photosynthesis (Weiss and Sauer, 1970; Witt et al.,1961 ; Parsons, 1968).

c. Time-Resolved Studies Using Ultrashort Laser Pulses.

Time-resolved spectroscopy with ultrashort laser pulses (Laubereau and Kaiser, 1978) involves the initial excitation followed by a series of weaker, appropriately time-delayed

probe pulses which do not overlap the excitation pulse. The excitation is either via direct resonant absorption or a laser beam shifted into the antiStokes region by a stimulated Raman process (Flynn and Sutin, 1974; Eckhardt et al., 1962). One then probes the fluorescence or Raman scattering from the sample to derive information regarding vibrational dephasing, orientational relaxation, energy transfer or relaxation (population changes), collective beating due to isotopic interference and a number of related dynamical processes in liquids.

The effects of hydrogen bonding of rhodamine 6G were studied in various liquids using a mode-locked Nd:glass laser (Chuang and Eisenthal, 1974). Orientational relaxation times were found to vary linearly with the viscosity; furthermore, the different hydrogen bonding in methanol and chloroform, which have the same viscosity, did not give rise to different relaxation rates, implying that, in the absence of aggregation effects, rotational motion of rhodamine 6G is independent of hydrogen bonding with the solvent.

Charge transfer is an important primary process in many reactions of biological interest. In a study of one such reaction $^1A + {}^1D \xrightarrow{h\nu} {}^1A^* + D \longrightarrow {}^1(A^-D^+)$ [A = anthracene, D = N,N'-diethylaniline], measurement of the differently polarized outputs resulting from a ruby laser excitation allowed a separation the effects due to orientational relaxation and complex formation (Chuang and Eisenthal, 1974, 1975). The results showed the transient portion of the electron transfer process to be in accord with the diffusion model of Smoluchowski or the Noyes

molecular-pair model (Noyes, 1961) at the earliest and intermediate times, while the long-time behavior corresponded to a steady state diffusion.

Evidence of the Franck-Rabinowitch cage effect in liquids was obtained in another application of time resolved laser spectroscopy (Chuang et al., 1974). For I_2 molecules excited by a Nd:glass laser, measurements of the intensity of the parallel and perpendicular components of the transmitted light as a function of time yielded geminate (i.e., involving the original atomic partners of an I_2 molecule in the same solvent cage) recombination times of 70 psec and 140 psec in hexadecane and CCl_4, respectively.

The study of vibrational relaxation rates of excited states in liquids is generally quite difficult. The use of an incoherent scattering technique makes such determinations possible, in some cases for the first time. Examples are the determination of the population lifetime T_1 of the 2939 cm^{-1} mode of 1,1,1 - trichloroethane (T_1 = 5.2 psec.) and a time-resolved study of intermolecular energy transfer from the above mode to the 2227 cm^{-1} mode of CD_3OD in a mixture of the two liquids (Laubereau, 1980).

2. Solids

While the effects of laser radiation on homogeneous systems in the gas phase, liquid phase or solid phase (Ready, 1971; White and Peercy, 1980) has been intensely studied, much less has been done on heterogeneous, e.g., gas/solid, gas/liquid and liquid/solid systems (Djidjoev et al., 1976; Karlov and Prokhorov, 1977; Goldanski

et al., 1976; Lin, 1980; George, 1980a-c; Lin and George, 1979a,b; 1980 ; Slutsky and George, 1978, 1979; Lin et al., 1980).

The current understanding of the nature of heterogeneous catalysis involves one or more of the following processes (Thomas and Thomas, 1967): (1) adsorption (physical or chemical) and desorption of the species on the catalytic surface; (2) migration of adsorbed species and subsequent collisions; (3) interactions (via dipole-dipole, electron transfer, etc.) between the adspecies, either directly or surface-mediated; (4) scattering (reactive or nonreactive) of gas-phase species by the clean surface or adsorbed species.

The effect of laser radiation on the above heterogeneous processes depends upon the nature of the surface (metal, insulator or semiconductor, smooth or rough, etc.), the electronic and vibrational structure of the adspecies/surface system and, of course, the frequency, intensity, fluence and polarization of the laser beam. Depending upon the physical and chemical state of the excited species, there are several possible ways in which laser radiation might influence heterogeneous processes. We shall discuss below some important types of laser-stimulated surface processes (LSSP) and related experimental and theoretical studies. (1) Laser excitation of reactants in the gas phase. The vibrational excitation of a molecule in the gas phase before striking a catalytic surface could lead to (i) an enhanced rate of reaction if the excitation energy can be used to overcome the reaction barrier, or (ii) a reduced rate of reaction due to decreased adsorption of the species on the catalytic surface. For example,

in the catalytic decomposition of formic acid over platinum (Ulmstead and Lin, 1978), the preexcitation of the gaseous formic acid molecules (by a 10 W/cm^2 CW CO_2 laser) resulted in a 50% increase in the ratio of the products CO_2/CO compared to that without the laser. Another study of LSSP of the first type (Tu et al., 1981; Chuang, 1980, 1981) showed that SF_6 vibrationally excited by CO_2 laser radiation was very reactive to silicon, and that the excitation of the silicon substrate alone could not cause the heterogeneous reaction to occur.

(2) Laser excitation of reactants adsorbed on a solid surface. A different kind of LSSP (Djidjoev et al., 1976, 1978) involves laser radiation directly incident on the surface of aerosil (SiO_2) in an ammonia atmosphere. Here the rate of decomposition of chemisorbed NH_2 groups in the radiation field of a low-power CO_2 laser (30 W/cm^2) was found to be three orders of magnitude larger than that in the corresponding thermal reaction.

(3) Laser heating of substrate. In addition to the selective-type excitations [types (1) and (2)], where the laser photon energy is deposited in a specific mode (or functional group) of the reactant, laser radiation may also be used for local heating of the substrate, and in turn influence the surface rate processes. A combination of the pyrolytic (substrate heating) and photolytic (dissociation of the reactant) reactions has been studied in laser-induced chemical vapor deposition (LCVD) with applications to microelectronics (Ehrlich et al., 1979, 1980a,b,c, 1981).

The above laser-matter interaction of heterogeneous systems involves the following fundamental mechanisms:

- How is the laser photon energy selectively transferred to the active mode of the species with subsequent relaxation to the bath modes (the inactive modes of the species plus the surface phonon modes)?
- What is the energy relaxation dynamics and the nature (selective and nonselective) of the energy deposition in the adspecies/surface system?
- How does the laser radiation affect the rate processes via field-induced adsorption, migration, diffusion, dissociation and desorption?
- How does the laser photon energy enhance the gas-solid interaction and change the thermal properties of the heated solid?

To describe theoretical techniques for addressing the above questions, we shall focus on the selective types (1) and (2) above and subsequently discuss nonselective types of LSSP involving LCVD and laser annealing (Section III.B.2.b).

a. Selective Excitation and Heterogeneous Catalysis

Here we shall discuss theoretical methods for describing energy transfer and bond breaking in terms of physical parameters including desorption probabilities, pumping rates, damping factors, etc., in connection with possible mechanisms for selective processes.

Consider a model system consisting of a group of adspecies driven by IR radiation. The microscopic Hamiltonian for the entire adspecies/surface system may be given as (Lin and George, 1979a; Lin et al., 1980)

$$H = H_A + H_B + H_{AB} + H_{AA} + H_{ABA} + H_{AF}, \qquad (18)$$

where H_A and H_B are the unperturbed Hamiltonians of the active (A) mode and the bath (B) modes, respectively and H_{AB} is the Hamiltonian describing the multiphonon coupling between the active mode and the bath modes. The terms H_{AA} and H_{ABA} represent direct and indirect interactions betwen the active modes, respectively. The last term H_{AF} represents the interaction betwen the active mode and the laser field. We note that the direct coupling term H_{AA} is related to the derivatives of the pairwise interaction potential between the adspecies with respect to the normal coordinates of the active modes (X_i). For example, in the case of a dipole-dipole interaction, the coupling constant is given by (Lin et al., 1980)

$$D_{ij} = (\alpha_i\alpha_j/2\bar{R}^3)(\partial\mu_i/\partial X_i)_0(\partial\mu_j/\partial X_j)_0, \qquad (19)$$

where μ_i is the dipole moment of the i-th active mode, $\bar{R}$ is the average distance between the dipoles (related to the adspecies coverage θ by $\bar{R} = 0.5\theta^{-2}$) and α_i is a quantization constant. The adspecies-field interaction Hamiltonian H_{AF} may be expressed in second-quantized notation as (Lin and George, 1979a)

$$H_{AF}(t) = [v_0(t) + v_1(t)(a^\dagger+a) + v_2(t)(a^\dagger+a)^2 + \ldots]\cos(\omega t), \qquad (20)$$

where the first term v_0 is related to pure rotational transitions while the remaining terms are related to rotation-vibration transitions for single-quantum, two-quanta, etc. processes and are characterized by the derivatives of the dipole moment.

In the Heisenberg-Markovian picture (Louisell, 1973), we are able to set up the quantum equations of motion for the average excitation of the active mode in which the many-body effects of the phonon bath modes (H_{AB} and H_{ABA}) and the active mode interaction (H_{AA}) may be replaced by single-body paramaters, namely, damping and dephasing factors and frequency shifts of the active mode. For a Markovian and adiabatic process, the coupled equations of motion governed by the total Hamiltonian in Eq. (18) reduce to a nonlinear differential equation for the average excitation <n> (Lin et al., 1980)

$$\frac{d<n>}{dt} = \frac{AI(\gamma_1+\gamma_2)}{(\Delta-2\varepsilon^{*}<n>)^2 + (\gamma_1+\gamma_2)^2/4} - \gamma_1(<n> - \bar{n}). \qquad (21)$$

$\Delta = \omega_A - \omega$ is the detuning, ω_A and ω being the frequencies of the active mode and the laser field (with intensity I), respectively; A is a constant proportional to the square of the derivative of the active-mode dipole moment evaluated at the equilibrium position; γ_1 and γ_2 are T_1(energy) and T_2(phase) relaxation rates induced by the many-body effects of the Hamiltonians H_{AA}, H_{AB} and H_{ABA}; $\bar{n}$ is a Bose-Einstein function for the bath modes; and $2\varepsilon^{*}<n>$ is the anharmonic correction.

Eq. (21) describes the conservation of energy of the total system (active and bath modes and laser field) with the following

important features: (1) the pumping rate is linearly proportional to the laser intensity for low excitations, although for high excitations, the anharmonic term leads to nonlinear behavior; (2) the energy relaxation rate for the active mode is governed only by γ_1 and not by the dephasing factor γ_2 whereas the absorption cross section is governed by the total broadening $(\gamma_1+\gamma_2)$; (3) the steady-state average excitation $\langle n \rangle^{s.s.}$ is given by a cubic equation which yields the power-dependence law $\langle n \rangle^{s.s.} \propto I^{\alpha}$, with $\alpha = 1$ and <1 for low and high excitations, respectively. Fig. 9 shows the average excitation as a function of laser intensity (Lin et al., 1980).

Fig. 10 shows the selective nature of LSSP via numerical solutions of the nonlinear Eq. (21). Another view of selective versus nonselective LSSP is presented in Fig. 11, where the results for a multilevel quantum system, obtained by solving for the energy populations in different modes (Lin and George, 1980b,c) are plotted. In these two figures the competition between the selective and nonselective aspects of LSSP is portrayed for a range of values of parameters such as pumping rates, damping rates and coupling constants.

We now discuss characteristics of systems exhibiting selective effects and surface-enhanced bond breaking. Let us consider a system whose vibrational degrees of freedom can be pictured as a set of distinct groups in the frequency domain. For simplicity, we shall consider the case of only two groups, A and B, where group A is referred to as the excited group consisting of the active mode plus other internal modes of the adspecies

coupled strongly to the active mode, and group B consisting of the remaining modes of the total system (adspecies plus solid). Depending on the relative magnitudes of the intragroup (R^{intra}) and the intergroup (R^{inter}) coupling rates, which characterize the energy randomization rate within and between the group(s), respectively, and the laser pumping rate (V), we may introduce several types of laser excitations: group selective, molecule-selective and purely thermal (nonselective). For LSSP to be characterized as group- or molecule- selective, the pumping rate must be greater than the energy relaxation rate(s), i.e., $V > R^{intra}$ and/or $V > R^{inter} >> R^{intra}$. For the case of very high pumping or low relaxation rates such that $V >> R^{intra}, R^{inter}$, a group-selective excitation would be possible. However, for low intensity excitations, group-selectivity seems less likely than molecule-selectivity since the only required condition is V, $R^{intra} >> R^{inter}$. According to the "energy-gap law", it is highly probable that a system have very weak intergroup coupling but strong intragroup coupling, examples being large molecules adsorbed on solid surfaces (SF_6/metal) or long chain adspecies (A-B-C-D/metal). In these systems the vibrational stretch of the excited species (which is not directly connected to the surface) may behave like a small subsystem, where the excited bond coordinate is composed of the normal coordinates of the related group. This selectively excited adspecies, while strongly coupled within the group, is weakly coupled to the remaining species (or functional group) of the system. Therefore, selective bond breaking of adspecies (or certain functional groups) will be

possible (Lin and George, 1981c).

Another important feature of selective bond breaking in a heterogeneous system (and usually not present in a homogeneous gas-phase system) is the surface-enhanced local field acting on the adspecies. The pumping rate could be enhanced by a significant factor when the local field is increased due to surface effects such as roughness and electron transfer involving the substrate. Using a simple relation between the pumping rate and the local electric field, $I \propto (E_{loc})^2$, we see that the magnitude of the laser intensity required for selective excitation may be reduced by a factor of 10^8 when the local electric field is enhanced by a factor of 10^4. We note that the enhancement by the local surface field (which explains surface-enhanced Raman scattering) can play an essential role in LSSP, where considerably lower laser intensities ($10\text{-}10^3$ W/cm^2) are used, compared to those for photodissociation of gaseous polyatomic molecules.

Given the absorption cross section [the first term of Eq. (21) divided by I], we can solve the master equation for the energy population to find physical quantities such as the laser-induced desorption probability, the desorption rate of the ad-species (or dissociation rate of the gaseous reactant) and the average excitations. Consider a heterogeneous rate process in which the overall reaction rate is limited by the removal of the product from the surface. The reaction rate then may be enhanced by laser-induced desorption of the product species. The desorption probability may be expressed in a simple Arrhenius form

$$P_D \propto \exp(-E_A/kT_{eff}) \tag{22}$$

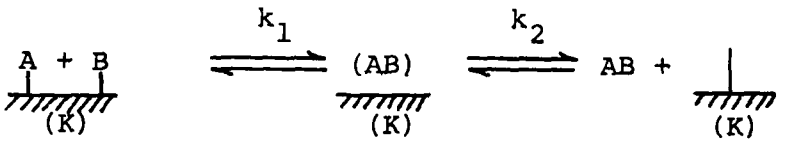
where E_A is the activation energy for bond breaking and T_{eff} is the vibrational temperature of the selectively-excited adspecies (product) given by $kT_{eff} \approx \langle N \rangle / S$, $\langle N \rangle$ being the average number of photons absorbed by the adspecies with S vibrational modes.

Another example of LSSP is where the reactant is vibrationally excited before sticking on the substrate surface. Here the overall reaction probability may be expressed as

$$P = P_V P_S P_R, \tag{23}$$

where P_V is the probability that the gaseous reactant is in the vibrationally-excited state accessed by the laser radiation, P_S is the (laser-enhanced) sticking probability of the excited reactant and P_R is the surface-catalyzed reaction probability. We note that $P \approx P_S$ when the sticking of the excited reactant is the rate limiting step, which may be greatly enhanced by the laser radiation. Furthermore, Eq. (23) can be used to describe a surface rate process where the dissociation of the gaseous reactant is the rate limiting step. In this case we replace the vibrational excitation probability by the dissociation probability given by Eq. (17).

We now turn to another interesting example of laser/surface-catalyzed rate processes, namely, the recombination of atoms A and B on a catalytic surface (K):



Laser radiation can influence the above reaction in several ways: (1) by increasing the mobility of the reactant atoms (A or B) through photon excitation of the A-K or B-K bond with subsequent enhancement of the reaction rate k_1; (2) by removal of the excess energy from the unstable complex (AB) on the substrate surface via laser-stimulated emission accompanied by surface-phonon-mediated relaxation thereby increasing the reaction rate k_2; and (3) by breaking the AB-K bound either directly through laser-excitation of the adspecies or indirectly through thermal desorption by laser-heating of the surface. We note that the direct desorption of chemisorbed species from a solid surface usually requires multiphoton absorption, necessitating the use of high-power radiation. However, much lower powers may be sufficient for the desorption of a diatomic molecule adsorbed on a solid surface (A-B-K) if the photon energy absorbed by the A-B molecule can be easily transferred to the surface to break the B-K bond via anharmonic coupling with the A-B-K system.

As a final example of LSSP, consider laser/surface-enhanced predissociation of a diatomic molecule adsorbed on a solid surface. It has been suggested that laser-induced predissociation of a gaseous species such as NO, CO and H_2 can be greatly enhanced by the presence of a surface magnetic field (Bhattacharyya et al.,

1980; Lin and George, 1981d). In these cases the magnetic field splits the electronic curves (other than singlet) of the "adsorbed" species into multiple branches, which gives rise to different dissociation channels and thus alters, the predissociation probability. One specific example with a ground singlet and an excited triplet is shown in Fig. 12. The dynamical probabilities of predissociation by a two-step excitation, namely, the absorption of one IR and one UV photon, is shown in Fig. 13 for the surface-phonon-coupled and surface-phonon-free cases.

b. Laser Applications to Microelectronics Fabrication

A new and rapidly developing field of laser applications is microelectronics fabrication at the large scale integration (LSI) and very large scale integration (VLSI) levels, the latter being associated with the development of very high speed integrated circuits (VHSIC) (Capece, 1978; Capece, 1979; Avery, 1980; Murphy, 1979). This new VLSI technology requires fabrication of Very Large Scale Integrated circuits, where line widths are reduced from the current 3 μm size of LSI to the submicron range and where one can have over a million devices on one chip (Smith et al., 1974; Lyman, 1980; Ratnakumar et al., 1980).

Since this exciting field is in its infancy, much of our discussion below should be viewed as suggesting the "potential" of laser photochemistry in microelectronics, rather than reviewing well-established techniques. Fabrication methods for LSI/VLSI involve the following steps (Fogiel, 1972):

1. Substrate preparation.
2. Lithography.
3. Oxidation/Passivation.
4. Diffusion/Doping
5. Epitaxy.
6. Chemical Processing.
7. Interconnection, lead attachment and packaging.

VLSI is still in the experimental phase, with a major portion of the effort aimed at solving the resolution problem at the lithography stage (Ratnakumar et al., 1980; Smith et al., 1974; Lyman, 1980; Decker and Ross, 1980). Some laboratories (Smith et al., 1974; Lyman, 1980) believe that the currently popular optical microlithography methods, which use masks in a contact or projection mode for LSI, can be improved for the submicron work of VLSI. Maskless techniques involving electron beams (and, less frequently, ion beams or X-rays), however, seem to be more promising alternatives for VLSI (Brewer, 1971; Smith et al., 1973, Spears and Smith, 1972; Broers and Hatzakis, 1972). No major changes in the technology for epitaxy are being proposed for VLSI, with chemical vapor deposition (CVD) being by far the most popular method for depositing thin films of a large variety of materials on substrates which are most often semiconductors or insulators (Feist et al., 1969; Shaw, 1975; Grünbaum, 1975; Kern and Ban, 1978). Recent experiments involving CVD have utilized laser radiation to control the reaction at various stages (Deutsch et al., 1979; Ehrlich et al., 1980a,b; Baranauskas et al., 1980; Allen and Bass, 1979; Christensen and Lakin, 1978; Steinfeld et al., 1980;

Fan et al., 1979; Gat et al., 1979; Williams et al., 1978; Sandow, 1980; Tamaru et al., 1980; Gibbons et al., 1979; Bean et al., 1978). In this review we shall concentrate on the CVD aspect of the fabrication process. However, other areas such as annealing will also be briefly discussed [Section III.B.2.b.(ii)].

(i) Chemical Vapor Deposition (CVD)

The generic processes occurring in CVD involve fundamental gas-surface interactions (Kern and Ban, 1978), the typical sequence of events being:

1. Diffusional transfer of gas particles (reactants) to the surface.
2. Adsorption of reactants on the surface.
3. Events on the surface, e.g., reactions, migration, lattice incorporation, etc.
4. Desorption of products from the surface.
5. Diffusion of desorbed species away from the surface.

The diffusion steps 1 and 5 are fairly well understood within frameworks such as the kinetic theory of gases (Geankopolis, 1972; Bird et al., 1960; Vanderputte et al., 1975) and generally do not represent critical points in the chemical process. Steps 2, 3 and 4 involving the actual gas-surface interaction are usually more important for the overall reaction, often include a rate-determining step, and form an area of active current research (Kern and Ban, 1978; Bryant, 1977). In

this context, results of model calculations of desorption dynamics (Doyen, 1980; De and Landman, 1980; Gortel et al., 1980a; Bendow and Ying, 1973; Efrima et al., 1980; Lin and Wolken, 1976a; Antoniewicz, 1980), phonon-induced surface migration (Efrima and Metiu, 1978; Prager and Frisch, 1980), elastic scattering (Lee and George, 1979c; Doll, 1974; Garcia et al., 1979; Goodman and Tan, 1973) and inelastic scattering (Shugard et al., 1977; Diebold et al., 1979; Tully, 1980; McCreery and Wolken, 1976; Lin and Wolken, 1976b; Diebold and Wolken, 1979; Milford and Novaco, 1971; Cole et al., 1979; Chow and Thompson, 1976), etc. have appeared in the literature. Experimental work in this area is dominated by surface spectroscopies such as IR (Eischens, 1972; Yates et al., 1979; Pirug et al., 1979; Evans and Wienberg, 1979), LEED (Ertl and Schillinger, 1977; Ibbotson et al., 1980), PES (Eberhardt and Himpsel, 1979; Oshima et al., 1979), Auger electron spectroscopy (Taylor et al., 1978) and EELS (Thiel et al., 1979; Baro and Ibach, 1979), which provide information about the geometry of the adsorption sites and changes in core electronic structure due to adsorption. Information on dynamics (adsorption/desorption, migration) of adsorbed species is obtained from temperature-programmed desorption (Tamm and Schmidt, 1969; Barford and Rye, 1974; Fair and Madix, 1980; Cohen and King, 1973), inelastic electron tunnelling spectroscopy, IETS (Ieb et al., 1979), FIM (Ertl, 1979), FEM (Stewart and Ehrlich, 1975) and mass spectroscopy (Brumbach and Somorjai, 1974; Bernasek and Somorjai, 1975; Palmer and Smith, 1974).

The range of CVD processes is almost unlimited, and

involves deposition of vitreous or crystalline forms of metallic, semiconducting or insulating materials on solids which span a similar range. Consequently, the variety of physical processes encompassed is also very extensive. Typical examples of CVD reactions include: the deposition of Si on Si by silane pyrolysis (Richman et al., 1970); GaAs on spinel, $MgO\text{-}nAl_2O_3$, $1.5 < n < 2.5$, by vapor-phase organometallic decomposition using trimethylgallium, $(CH_3)_3Ta$, and arsine, AsH_3 (Wang et al., 1974); SiO_2 on Si by oxidation of tripropylsilane, $(C_3H_7)_3SiH$ (Avigal et al., 1974); and W on Si by hydrogen reduction of WF_6 or WCl_6 (Melliar-Smith et al., 1974). Other CVD reactions can be found in a recent review (Kern and Ban, 1978). While alternative methods of depositing thin films of different materials on solid substrates are available (Vossen, 1978), for example, molecular beam epitaxy, eletrrodeposition, sputtering, direct transport of vaporized materials, plasma anodization, ion implantation, liquid-phase epitaxy, etc., CVD is by far the most important method for epitaxial growth from a commercial point of view because of atmospheric pressure operation, ease of doping, the almost unlimited number of reactions and starting materials available, and many other advantages (Feist et al., 1969; Shaw, 1975). However, the high temperature often required for the reactions and the toxic, corrosive or explosive nature of the reactants involved in CVD leads to problems such as undesirable diffusion, alloying or chemical reactions and contamination or corrosion of substrate and deposit films. Byproducts of the reaction (such as polymers) may also attack or settle in the apparatus. In many cases, there

are also difficulties associated with the control of the growth rate and masking processes. Finally, the stresses imposed on the substrate by strong temperature gradients lead to softening, warping and other defects which are responsible for an unusually high rejection rate of the mass-produced circuits (Lyman, 1977; Kamins, 1974; Auston et al., 1979).

The recently initiated use of lasers in microelectronics fabrication presents some very exciting possibilities for overcoming some of the problems in conventional CVD. Thus, for example, the application of lasers in the annealing of amorphous films in some CVD reactions (Tamaru et al., 1980; Gibbons et al., 1979; Bean et al., 1978) or damaged surface layers resulting from ion-implantation (Fan et al., 1979; Gat et al., 1979; Williams et al., 1978; Auston et al., 1979) via solid-phase or liquid-phase epitaxy seems to be fairly well established as an industrial process. A somewhat less-established application involves the initial deposition of chemically produced elements or compounds in a laser-stimulated gas-phase reaction. In recent experiments (Deutsch et al., 1979; Ehrlich et al., 1980a) a UV laser beam of wavelength 257.2 nm was used to break specific molecular bonds in gaseous trimethylaluminum, $(CH_3)_3Al$, and dimethylcadmium, $(CH_3)_2Cd$, from which Al or Cd, respectively, were deposited on a quartz substrate. These experiments represent a radical departure from the conventional laser processing techniques involving only thermal effects such as annealing or laser heating of the substrate (Baranauskas et al., 1980; Allen and Bass, 1979; Christensen and Lakin, 1978) in CVD. More recently the feasibility of combining both the

thermal and nonthermal laser processing techniques in CVD was clearly demonstrated (Ehrlich et al., 1980b). The use of a focused laser beam (2-3 μm) in these experiments results in a strong localization of both the deposition process and the surface heating, thereby obviating the need for high temperatures throughout the reaction chamber. Some of the problems associated with the high temperature could thus be minimized by the use of lasers.

The revolutionary potential of the combined thermal-plus-nonthermal laser processing technique becomes clear when it is realized that effectively the lithography and deposition steps, which have traditionally been independent and sequential (Fogiel, 1972) can thereby be combined into one step. Serious development of this technique holds forth the promise of eliminating whole steps from the fabrication line, leading to substantial economies and simplifications in the microelectronics technology.

We mention in passing the possible use of visible or UV (V/UV) lasers as lithographic tools (scribes). [Assuming the extent of the limiting focal region to be about the same as the wavelength of the light, infrared lasers would be quite ineffective for VLSI (submicron) lithography.] Finely focussed V/UV laser beams of this nature will function mainly as sources of very high local temperatures, and lithography would primarily involve vaporization (or melting) on the solid surface.

An analysis of the common CVD reactions (Kern and Ban, 1978) provides meager but interesting insights into the nature of some important mechanisms involved in deposition. Growth

rates are seen to be sensitive to temperature, orientation, the form of carrier gas, and of course the nature of the substrate; the sensitivity furthermore varies over a large range depending on other conditions. Thus, for example, the temperature dependence of the deposition rate is weak if the rate-determining step is the diffusional transport of reactants in the gas phase to the surface, since the diffusion constants are almost independent of temperature (Geankopolis, 1972; Bird et al., 1960; Vanderputte et al., 1975). However the temperature dependence is strong if the rate is determined by a step in a surface reaction (Joyce and Bradley, 1963; Farrow, 1974) such as, for example, the rate of desorption of hydrogen produced by the decomposition of silane on a silicon substrate. This is a particularly clear example of a situation where the selective laser-stimulation of a single phase of a reaction could increase the overall rate. Thus, by pumping the hydrogen-to-surface bond with low-power infrared laser radiation of the "right" frequency, the rate of hydrogen desorption could be enhanced, and higher deposition rates could be achieved at much lower temperatures. Desorption could conceivably also be enhanced by exciting the system electronically using higher-frequency laser radiation. However, the mechanism in this case is not quite as clear, and the selectivity might not be as sharp.

The diverse dependences of deposition rates on the nature of the substrate and the orientation of the crystal face represent a more difficult situation (Kerr and Ban, 1978). A variety of mechanisms can be invoked to explain the variations in the

deposition rate, some of them interrelated. Thus, (a) lattice mismatch between the film and the substrate can lead to dislocations and poor growth rates. (b) the charge-density variation on the surface changes dramatically when different lattice planes are exposed as also the concentration of dangling bonds (i.e., the degree of unsaturation on the surface), so that the layer thickness at which the influence of the substrate surface disappears and steady-state epitaxy sets in is also dictated by the exposed lattice plane. (c) Some crystal planes permit a larger number of intrinsic defects which can enhance deposition if they act as active sites for catalytic initiation of a reaction step, or de-enhance deposition if a smooth surface is required for growing single-crystal films of products condensing from a gas-phase reaction. (d) In the final analysis, variations in the nature of the surface potential (both normal and parallel to the surface) at different crystal faces lead to differences in the dynamics of adsorption, desorption, migration or even lattice incorporation or penetration. It is likely that one or more of these processes represents a bottleneck for the rate of deposition, and a clear understanding of the connection between the two could lead to improved efficiencies for the CVD reactions.

An important class of CVD reactions involves "selective" deposition (Berkenblit and Reisman, 1971; Engeler et al., 1970), where the film growth takes place only on one part of the substrate due to different sticking coefficients on the different materials constituting the substrate. The depositions of silver and tungsten described earlier (Melliar-Smith et al., 1974; Shaw and

Amick, 1970; Voorhoeve and Merewether, 1972) are two examples of such a process; the metals deposit only on the silicon exposed through a layer of deposited silicon oxide, while the oxide is only mildly etched. Selective deposition of semiconductors has also been exploited for growing epitaxial germanium on small areas of Ge or GaAS substrates (Berkenblit and Reisman, 1971), and (in the "epicon" TV camera tube structure) growing pyramidal-shaped structures of p-type silicon on top of a patterned oxide-covered wafer of n-type silicon (Engeler et al., 1970). The latter structures are nucleated only on silicon and grow up through apertures in the oxide layer. Each structure forms a capacitor: an oxide layer sandwiched between layers of n- and p-type silicon.

Selective deposition is taken one step further in the so-called "electroless plating" by selective deactivation (Feldstein and Lancsec, 1970; Paunovic, 1980). Here the surface is chemically prepared using a two-step adsorption/chemical replacement technique which results in a layer of catalytic palladium on a photoresistively patterned surface. The activated substrate is then etched, causing selective deactivation, and finally plated along the active regions.

It is possible to conceive of a laser playing the role of selective activator of deactivator. By causing disturbances in specific vibrational or electronic energy transfer processes involved in adsorption, desorption or migration of a gas atom or molecule on a surface, sticking probabilities can be altered. Use of high-power lasers as sources of local heating is not expected to be effective in this mode since all degrees of free-

dom would be equally favored. However, relatively low-power lasers with frequencies and linewidths chosen properly can be expected to interact strongly with a single vibrational or electronic degree of freedom (or, alternatively, with a very narrow band of such states). Whether this guarantees selective surface activation or deactivation depends crucially on an understanding of the nature of the time evolution of the gas-surface system in regard to energy transfer between the adspecies and the solid and among the adspecies themselves. Other important elementary processes include migration, desorption, transitions of the adspecies between some precursor (perhaps physisorbed-) state and a chemisorbed state, changes of adsorption site (for example, to one where the adspecies is not laser-active), surface collisions and reactions, charge-transfer processes, and the arrival of more gas-phase species at the surface (leading eventually to a complete monolayer and, subsequently, multilayer formation).

The kinetics of processes taking place on the surface can be separated into two components:

(i) the kinetics of adsorption of the first few atoms or molecules to reach the surface; and

(ii) the kinetics of subsequent multilayer formation.

The theoretical problem associated with multilayer formation is not well defined at this stage. It is, of course, the next logical step after initial deposition begins, and as such is an important component of the overall CVD reaction. However, it represents a set of fundamentally different processes from those involved in the initial adsorption and is more closely related

to homogeneous crystal growth (or agglomeration of microcrystallites, if actual epitaxy is not being considered).

In many cases of CVD, the fundamental reaction (for example, the decomposition of metal alkyls) actually takes place in the gas phase, with the desired material then condensing on the substrate. The stimulation of such gas-phase reactions by laser radiation is being actively studied (George et al., 1979; George, 1979; Zewail, 1980; Letokhov, 1980; Zare and Bernstein, 1980; Lee and Shen, 1980). Outstanding problems here are associated with intermolecular energy transfer processes which have a direct bearing on the ultimate destination of the laser energy and hence the nature of the final states of the gas molecules (dissociation, ionization, formation of excited intermediates, thermal randomization, etc.). A study of these gas-phase processes is important for a variety of reasons. The formalisms used for the study of gas-surface processes are often closely related to techniques used in gas-phase studies, often being extensions or modifications of the latter; also, the gas-phase reactions form an important part of the overall CVD process, one which can easily be treated with present-day techniques.

The laser can interact with the gas-surface system in three ways: direct pumping of the gas-phase species alone, pumping of the adspecies-substrate system, and interaction with collisional dynamics leading to the actual adsorption. The last way is particularly intriguing from a theoretical point of view, but the laser intensities required are too high from a practical standpoint (Lee and George, 1979a,b; George et al., 1980). The other

two are intimately involved in LCVD for reasonable laser intensities.

Laser interaction with the gas phase can involve the following processes:

(a) Excitation (rotational, vibrational or electronic) and/or ionization.

(b) Dissociation into ionic or atomic fragments.

(c) Thermal effects (e.g., increasing average kinetic energy).

This aspect (gas-laser interaction) has received considerable theoretical attention in the past and continues to be an active field of endeavor with many outstanding problems.

Laser-stimulation of adspecies-surface interactions includes analogous processes:

(a) Preparing the adspecies or the surface in a particular state.

(b) Adsorption/desorption of neutral or ionized fragments; dissociation of the adspecies.

(c) Thermal effects (e.g., increased mobility on the surface).

Phonon Band Structure and Infrared LCVD. When a molecule is adsorbed on a surface, it can exchange vibrational energy with the solid via the bond with the nearest atoms of the solid. The nature of this interaction will have a direct bearing on whether the molecules stays on the surface at a given site, moves around on the surface, or is desorbed. In conjunction with the electronic mechanisms described later in this review, this multiphonon

vibrational relaxation dictates the nature of the kinetics of deposition of specific adspecies.

In general, the response of the system to infrared radiation is quite complex, involving a large number of degrees of freedom, which are often quite different from those of the isolated adspecies or solid. The monochromatic nature of laser radiation holds the promise of simplifying the situation by separating out a few (often just one) degrees of freedom which are influenced more by the field than the others because of a resonance or near-resonance condition. An example is the case of an adsorbed molecule with one of its vibrational modes (A) having a fundamental frequency very close to that of the laser. If none of the other vibrational modes of the molecule (B) or phonon modes of the solid (C) are close to the laser frequency, the electromagnetic energy is primarily absorbed by the A mode (the active mode), and the B and C modes act as "bath" modes from a thermodynamic point of view.

Theoretical Treatments of Desorption. A variety of methods have been applied to the problem of desorption, in particular phonon-stimulated desorption. Inclusion of the effects of laser radiation has been attempted only recently (Lee and George, 1979a,b; George et al., 1980; Lin and George, 1980a,b,c,d; Lin and George, 1979; Lin et al., 1980; Slutsky and George, 1978, 1979; Bhattacharyya et al., 1980; Murphy and George, 1981). The theoretical treatment of relaxation phenomena (Zwanzig, 1960), is based on either (1) a classical Liouville equation, namely

$$i \frac{\partial f(\vec{r},\vec{p},t)}{dt} = Lf(\vec{r},\vec{p},t) \quad , \tag{24}$$

where f is the phase-space ensemble density, $\vec{r}$, $\vec{p}$ and t represent the totality of coordinates, momenta and time, respectively, and L is the classical Liouville operator

$$L = i \frac{\partial H}{\partial \vec{r}} \frac{\partial}{\partial \vec{p}} - i \frac{\partial H}{\partial \vec{p}} \frac{\partial}{\partial \vec{r}} \tag{25}$$

with H the classical Hamiltonian for the system; or (2) a quantum mechanical equation of motion such as the Heisenberg equation

$$i \frac{\partial \rho}{\partial t} = \hbar^{-1}(H\rho - \rho H) \quad , \tag{26}$$

where ρ and H are the quantum mechanical density matrix and Hamiltonian operator, respectively. Within these basic frameworks, previous investigations are distinguished by the natures of the approximations employed in constructing H or L and in solving the equations of motion. The following are some of the more common techniques currently in use:

(i) Direct solutions of Heisenberg's equation of motion (Doyen, 1980; De and Landman, 1980; Gortel et al., 1980; Lin and Wolken, 1976a, Antoniewicz, 1980; Shugard et al., 1977; Diebold et al., 1979; Tully, 1980; Beeby and Dobrzynski, 1971; Holloway and Jewsbury, 1976; Holloway et al., 1977; Wolken and McCreery, 1978; Nitzan and Jortner, 1972; Nitzan et al., 1974; Nitzan and Silbey, 1974; Gortel et al., 1980b), some of which assume random-phase or Wigner-Weisskopf approximations.

(ii) Solutions of Liouville's equation using projection operator techniques, developed by Mori, Kubo and Zwanzig, closely related to the generalized Langevin equation (Diestler and Wilson, 1975; Lin and Adelman, 1978; Shugard et al., 1978; Nitzan et al., 1978).

(iii) Solutions of a generalized master equation for the population of the various modes of the system subject to a stochastic force (Müller and Brenig, 1979). The assumption of Markovian statistics simplifies the solution, but non-Markovian problems have also been treated recently (Grigolini, 1979).

(iv) A formalism developed by van Hove and Glauber which leads to expressions involving "time- and position-dependent displacement-displacement correlation functions" for the phonons (van Hove, 1954; Glauber, 1955) but which is somewhat difficult for actual computational purposes (Bendow and Ying, 1973).

(v) A Green's functions approach (Tapilin et al., 1978; Allen, 1979a,b).

(vi) The CCGM approach (Cabrera et al., 1970; Garcia et al., 1979; Goodman and Tan, 1973).

(vii) A surface band-structure approach (Milford and Novaco, 1971; Cole et al., 1979; Chow and Thompson, 1976; Tsuchida, 1968; Wolken, 1974; Gerber et al., 1978).

In almost all these cases, the Born approximation is invoked, transition rates are calculated using the Fermi Golden Rule expression, and the solid is treated within a Debye model. The

aspects in which the above treatments differ include:

(a) Type of surface potential used, e.g., truncated harmonic oscillator, square well, spherically symmetric Morse or Lennard-Jones, anisotropic (angle-dependent) Morse or Lennard-Jones, single potential function for outermost surface atom and adsorbed atom, or a sum of pair potentials between the adatom and atoms of the solid.

(b) One-dimensional (linear chain) or three-dimensional treatment.

(c) Second-order perturbation theory or fourth-order perturbation theory.

(d) No-phonon, one-phonon, two-phonon or multiphonon processes included in gas-solid energy transfer.

(e) Band-structure effects due to two-dimensional periodicity of the surface included or ignored.

(f) Classical trajectory or classical normal-mode treatments versus quantum mechanical calculations of expectation values using suitable basis sets.

(g) "Local oscillators" versus "delocalized oscillators" ("phonons") treatment of the solid.

(h) Adsorption potential with one bound state or a large number of bound states.

Different combinations of these options are necessary or sufficient for different systems, and broad consensuses as to relative merits are generally lacking. Thus, for example, a one-dimensional model seems to be sufficient for many problems

involving physisorption (Beeby and Dobrzynski, 1971; Holloway and Jewsbury, 1976; Holloway et al., 1977; Gortel et al., 1980b; Goodman and Romero, 1978). However, due to the small number of investigations aimed at chemisorption, no such indication exists for the case of strong bonding. The situation regarding multi-phonon effects is also fraught with controversy. In the past, the intuitively attractive idea that one-phonon processes suffice if $E_0<\hbar\omega_D$, two-phonon processes if $\hbar\omega_D<E_0<2\hbar\omega_D$ (where ω_D is the Debye frequency and E_0 represents the position of the lowest bound state of the adspecies with respect to the adsorption continuum) and so on, was generally accepted. However, recent work (Jedrzejek et al., 1981) suggests that N-phonon processes (N>>1) may always be important, pointing out a possible problem of convergence criteria and perhaps the necessity of abandoning perturbation-theory approaches in favor of direct solutions of the problem. The latter is computationally very difficult, and it is necessary to adapt existing theories to each specific problem.

The choice between local oscillators versus lattice normal modes (phonons) represents a very fundamental problem (Lin and Wolken, 1976a, Antoniewicz, 1980). In the case of atom-surface scattering, a phonon treatment seems appropriate for collision times τ much larger than the characteristic time for energy dissipation in the solid, and a local modes treatment for the opposite case. However, in the case of adsorbed atoms or molecules, where a corresponding "residence time" is often unknown, such clear distinctions are difficult.

The foregoing represents a survey of theoretical tech-

niques that are currently employed in treating the adspecies-surface interaction. Specific approaches that are being used in this laboratory include methods (i), (ii) and (iii) mentioned earlier in this review and discussed further below:

(i) By employing the Wigner-Weisskopf (or random-phase) approximation (Louisell, 1973) one can decouple the phonon modes from the active mode, and the many-body effects of the phonon couplings may be reduced to a Fermi-type damping factor which is characterized by the phonon density of states. The advantage of this technique is that the many-body quantum system is thereby reduced to a one-body problem where the average excitation of the active mode is calculated including nonlinear effects (Lin and George, 1980d; Lin et al., 1980) and migration-induced broadening (Slutsky and George, 1978, 1979).

(ii) Instead of using the quantum approach in (i), one may use a classical approach. One can, for example, employ the generalized Langevin equation (GLE) to describe the dynamical behavior of the excitation processes. Solution of the GLE provides a lineshape function (or an absorption cross-section) in a more general form which involves T_1 (energy) and T_2 (phase) relaxations and memory effects (Lin and George, 1980d, 1981a,b). This technique provides phenomenological results to which parameters such as the total width of the lineshape can be semiempirically fitted.

(iii) By knowing the transition rate or the absorption cross section which are calculated by the techniques in (i) and (ii), one is able to solve a generalized master equation

(GME) in photon energy space (George et al., 1980). The energy populations (which are solutions of the GME) provide one with important information such as the photodissociation probability and the nature of the laser excitations - selective or non-selective (Lin and George, 1980a,b; Lin et al, 1980; Lin and George, 1980).

Photon-Stimulated Charge Transfer on Surfaces. In semiconductors, the electronic band structure can be very complicated. The effects of exposure to laser radiation, however, can be readily evaluated using simplified wave functions and time-dependent perturbation theory (Pidgeon et al., 1979; Lee and Fan, 1974). These techniques can also be applied to a study of photon absorption and associated charge-transfer processes in the surface region.

Surfaces introduce additional features (Lundquist, 1975) into the bulk electronic band structure of solids. In addition to the bulk valence bands and conduction bands, there can exist surface bands. Furthermore, defects and adsorbed species can introduce additional bands and localized states. Fig. 14 is a simple schematic of what this band structure might look like.

There may actually be several bands introduced by the surface, which fall in various places in the band structure. However, one can assume that in the solid under investigation there is one surface band, S, and local states, represented by dashes, which fall in the bulk energy gap.

Electrons which have the energy associated with the surface band will be localized in the surface region. Similarly,

electrons with energies corresponding to the local states will be localized in the region of the adsorbates or the defects which produced these states. On the other hand, the electrons located in the conduction and valence bands are essentially delocalized throughout the solid.

With a laser appropriately chosen (IR to visible) to excite electrons from a local adsorbate state to the conduction band or from the valence band to the local adsorbate state, the area around the adsorbed species can be made effectively more positive or negative. This charge difference can lead to a strong Coulomb interaction. By choosing the appropriate charge concentration, this process could be used to selectively clean the surface of contaminants. A laser can be used to excite the local states created by the contaminants without affecting the states associated with desired adsorbates. In fact, photon-stimulated desorption has been observed at the surface of a variety of metals (Woodruff et al., 1980; Jaeger et al., 1980). Although the desorption process is somewhat different from the one described here (Knotek and Feibelman, 1978), the main cause of the desorption is the Coulomb repulsion between the adsorbate and the surface.

If one is attempting to react different species on the surface, one can also use the solid as a charge bath. One can excite an electron into a local state induced by one species and excite an electron out of a local state induced by another species. Hence, even if the two species are far apart, by using the solid bands as intermediaries one can induce an effective

charge transfer between species. The resultant adsorbates may then be in the ideal state for interaction with other species being deposited.

(ii) Annealing

Here we discuss a technologically important application of a nonselective thermal type of LSSP [see the beginning of Section III.B.2]. The influence of high-power radiation on matter in the solid phase has been of interest for over a decade (Ready, 1971). However, laser annealing of semiconductors has only recently been explored in connection with microelectronics (White and Peercy, 1980). Laser annealing originally focused on the removal of defects introduced by ion implantation. Its scope has recently been broadened to include the transient heating of semiconductors, where lasers now provide a rich new range of opportunities for studying fast crystalline growth involving both solid and liquid phase epitaxy.

In an attempt to describe laser heating of solids, one seeks solutions to the heat-conduction equation, which, for the case of one dimension, is usually given as (Carslaw and Jaeger, 1959)

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[D(T) \frac{\partial T}{\partial x}\right] + S/c\rho \ , \qquad (27)$$

where D(T) is the thermal diffusivity (in general temperature dependent), and c and ρ are the specific heat and mass density, respectively. The local heating rate is governed by the source

term S given by

$$S(x,t) = I(t)(1-R)g(x), \tag{28}$$

where I(t) represents the laser intensity, and R and g(x) are the reflectivity and diffusion factor, respectively. The diffusion factor accounts for the laser-generated charge carriers and reduces to the usual Beer's law form $g(x) = \exp(-\alpha x)$ for the case of long lifetimes of the carrier diffusion, where α is the optical absorption coefficient (Yoffa, 1980a,b).

The above heat transport equation cannot, in general, be solved analytically due to the temperature dependence of the thermal diffusivity D(T). The thermal properties of the laser-heated solid are characterized not only by the solid itself but also by the types of laser radiation. For example, in pulsed laser annealing of semiconductors, a liquid layer is thought to form during the annealing process, and the redistribution of dopants is explained by using a model based on the diffusion of dopants in liquid silicon (Baeri et al., 1978). On the other hand, a scanning CW laser can produce solid-phase recrystallization of the implanted layers, with no diffusion of implanted dopants during the annealing cycle (Liau et al., 1979).

For the interaction of radiation with solids, there is controversy regarding the main physical mechanisms responsible for annealing, namely thermal melting models versus nonthermal ones (Van Vechten et al., 1979; Lo and Compaan, 1980; Kim et al., 1981). The expression for the local lattice temperature of the solids consists of a laser heating term and a term corresponding

to energy flux due to thermal diffusion. For materials with a large thermal conductivity which is weakly dependent on temperature, the effect of carrier diffusion on the rise of the lattice temperature may not be important. On the other hand, when the thermal conductivity decreases sharply with increasing temperature, the carrier diffusion plays an important role. For the case of silicon, the carrier diffusion does lower dramatically the heating efficiency near the surface. For a more detailed understanding of transient laser-induced processes in semiconductors, a study of the relative time scales of processes such as electron-electron, electron-phonon and electron-hole interactions and the electronic structure of the material (Brown, 1980), is necessary.

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Figure Captions:

Fig. 1. Two schemes of selective multistep photoionization of atoms by laser radiation: a) two-step photoionization; b) two-step ionization via an autoionizing state.

Fig. 2(a). Two-step (IR+UV) photodissociation. The IR photon accesses an excited vibrational level of the ground electronic state and the UV photon then accesses the excited electronic state on which the molecule dissociates.

Fig. 2(b). One-step photo-predissociation. A UV photon accesses an excited vibrational level in an excited electronic state which crosses an excited repulsive electronic state. Dissociation occurs through the coupling near the crossing.

Fig. 3. The universal energy absorption profiles of the pumped mode for different sets of the optimum detuning Δ_{opt} and the damping factor γ (in units of cm^{-1}): curve A - $\Delta_{opt}=0$, $\gamma=2\times10^{-3}$; curve B - $\Delta_{opt}=0.5\gamma = 5\times10^{-4}$; curve C - $\Delta_{opt}=\gamma=10^{-3}$; curve D - $\Delta_{opt}=2.5\gamma=2.5\times10^{-4}$; curve E - $\Delta_{opt}=5\gamma=2\times10^{-5}$; curve F - $\Delta_{opt}=8\gamma=10^{-5}$; curve G = $\Delta_{opt}=10\gamma=10^{-4}$; for low-power laser $I=100W/cm^2$. Note that the time scales are shown in units of γ^{-1}. From Lin and George, 1980a.

Fig. 4. Log-log plot of the intensity dependence of three-photon ionization in cesium at the ruby-laser frequency. From Georges and Lambropoulos, 1977.

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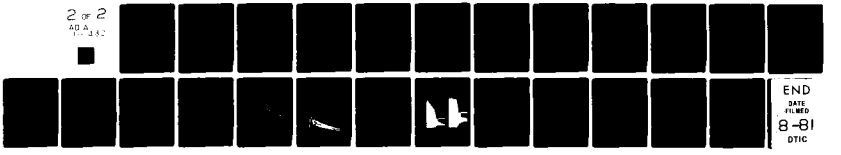


Fig. 5(a). The distribution functions of four-photon excitations $\langle n \rangle = 4$, for Poisson population (- -), diffusion model population with S=1 (-·-) and S=6 (----), Boltzmann population with S=1 (-··-) and S=6 (-), and quantal population with $S = \alpha = 1$ (-···-).

Fig. 5(b). The desorption probabilities of $n^*=5$ for Poisson distribution (- -), diffusion model with $\beta=1$, S=6 (---), Boltzmann distributions with s=6 (-··-) and S=1 (-), and quantal model with $\alpha = S = 1$ (-···-).

Fig. 6. Two viewpoints of looking at the collision-induced absorption of a photon. Δ is the detuning. In the separated-atom-limit picture (represented by the wavy line at the right), the photon is not in resonance with the energy levels, collisional effects make up for the detuning energy. In the molecular picture (represented by the wavy line on the left) the resonance requirement is fulfilled at a finite internuclear separation. Note that the wavy lines are of the same length - represening a photon of the same frequency.

Fig. 7. A sketch of two model nonreactive electronic surfaces W_1 and W_2 plus their shifted images $W_1 + \hbar\omega$ and $W_2 + \hbar\omega$(a) and the resulting electronic-field surfaces E_0, E_1, E_2, and E_3 obtained from them (b). This figure illustrates the utility of the electronic-field approach in clarifying the dynamical behavior of a more complicated scattering system undergoing irradiation.

Fig. 8. A sketch of three model electronic surfaces, one of which (W_1) is reactive, plus the shifted image $W_1 + \hbar\omega$ of the reactive surface (a). If the dynamical coupling of the corresponding electronic states is negligible, then the relevant electronic-field surfaces are those illustrated in (b). Here, E_1 correlates to W_2 asymptotically far to the right, E_2 similarly correlates to W_3, and E_3 to $W_1 + \hbar\omega$. It is evident that the intense field can greatly inhibit reaction for this system when the initial electronic state corresponds to W_1, while assisting reaction from W_2 and (to a lesser extent) W_3.

Fig. 9. Maximum excitation X* vs laser intensity | under the optimal detuning condition for $\gamma_1 = 10^4 s^{-1}$, $\gamma_2 = 10cm^{-1}$, and (A) $\varepsilon^* = 1cm^{-1}$, (B) $\varepsilon^* = 2cm^{-1}$, (C) $\varepsilon^* = 3cm^{-1}$, and (D) $\varepsilon^* = 5cm^{-1}$. The resonant harmonic excitation ($\varepsilon^* = \Delta = 0$) is shown by dashed line. From George et al., 1980.

Fig. 10. Average selective excitation number $\langle N_s \rangle$ (the energy difference between the active mode and the bath modes) as a function of time t for various values of the energy relaxation rate γ_1: (A) $10^2 s^{-1}$; (B) $10^3 s^{-1}$; (C) $2 \times 10^3 s^{-1}$; (D) $6 \times 10^3 s^{-1}$; and (E) $10^4 s^{-1}$. Values of the other parameters are: $\gamma_2 = 10cm^{-1}$, $\Delta \equiv \omega_A - \omega = 24.9cm^{-1}$, $\varepsilon^* = 2cm^{-1}$ and the laser intensity $I = 10\ W/cm^2$. We note that curves A and B represent the highly selective

(Continued)

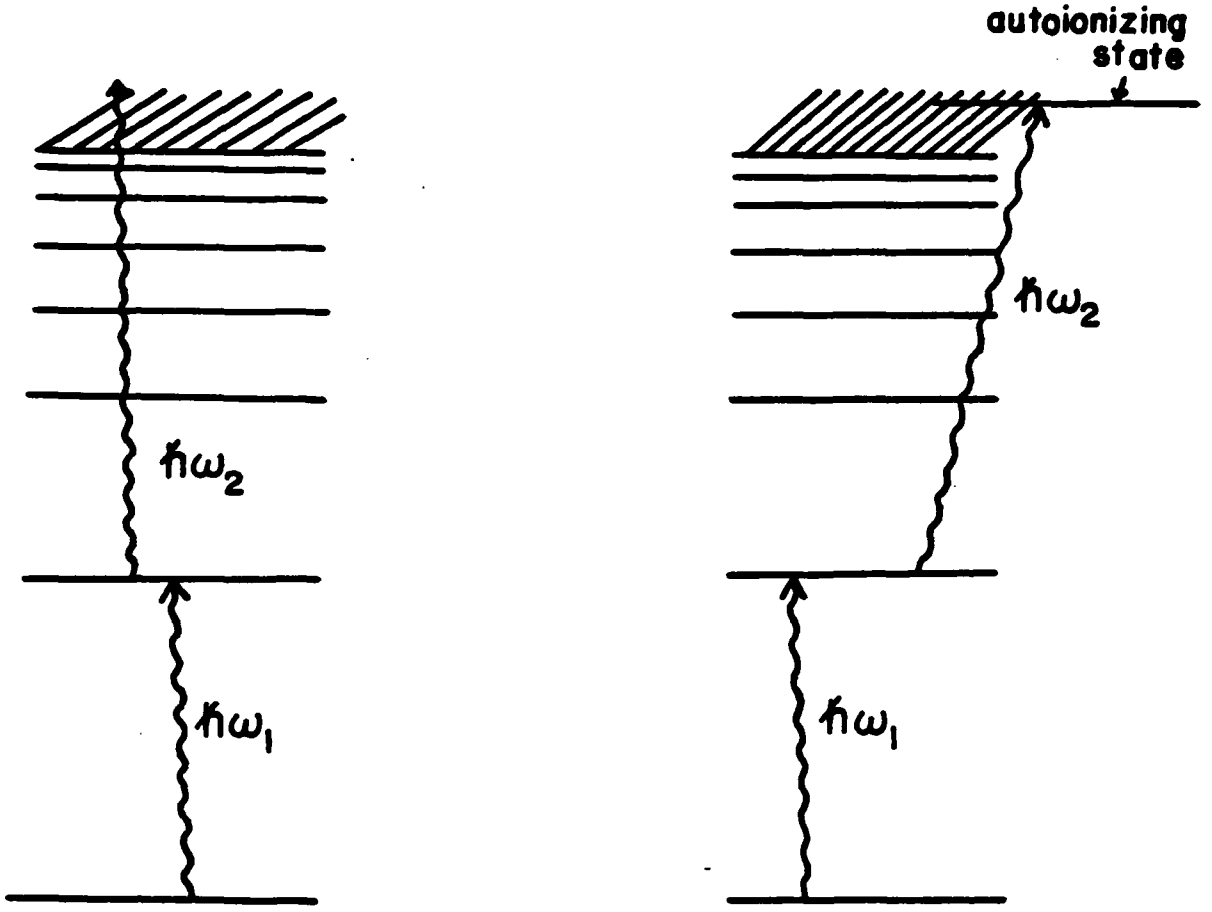
Fig. 10. excitations while curve E represents the nonselective excitation. From Lin et al., 1980.

Fig. 11. The level populations of the active mode (P_A) and the bath modes B(P_B) and C(P_C) of two-photon multiphonon processes for the pumping rate (V), coupling factor (g), and damping rates (γ) given by (V,g,γ) = (A) (4,0.1,0.4), and (B) (4,1,1). Note that (A) shows the highly selective excitation of the active mode with high P_A and low P_C while (B) shows the nonselective thermal excitation of the C modes with high P_C and low P_A. From Lin and George, 1980d.

Fig. 12. Schematic energy diagrams of a multilevel-multistate system subject to two lasers with frequencies ω and ω', respectively. Note that the electronically excited triplet state is split by the surface magnetic field.

Fig. 13. The time evolution of the energy populations of the active mode (P_A), the phonon (bath) modes (P_B) and the predissociation probability (P_D) for (V,G,γ,Δ,α) = (A) (10,1,0.1,0,1) for a phonon-coupled and (B) (10,1,0,0,1) for a phonon-free system. V,G,γ,Δ and α are the pumping rate, the Landau-Zener factor, phonon-induced damping, the field detuning and the phase detuning, respectively. From Lin and George, 1980f.

Fig. 14. Schematic representation of the electronic energy-level band structure of a semi-infinite solid. Allowed energy levels are given as functions of wave-vector $\vec{k}$ along a fixed direction in the first Brillouin zone. CB - conduction band; VB - valence band; S - surface states; E_g - energy gap.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(a)
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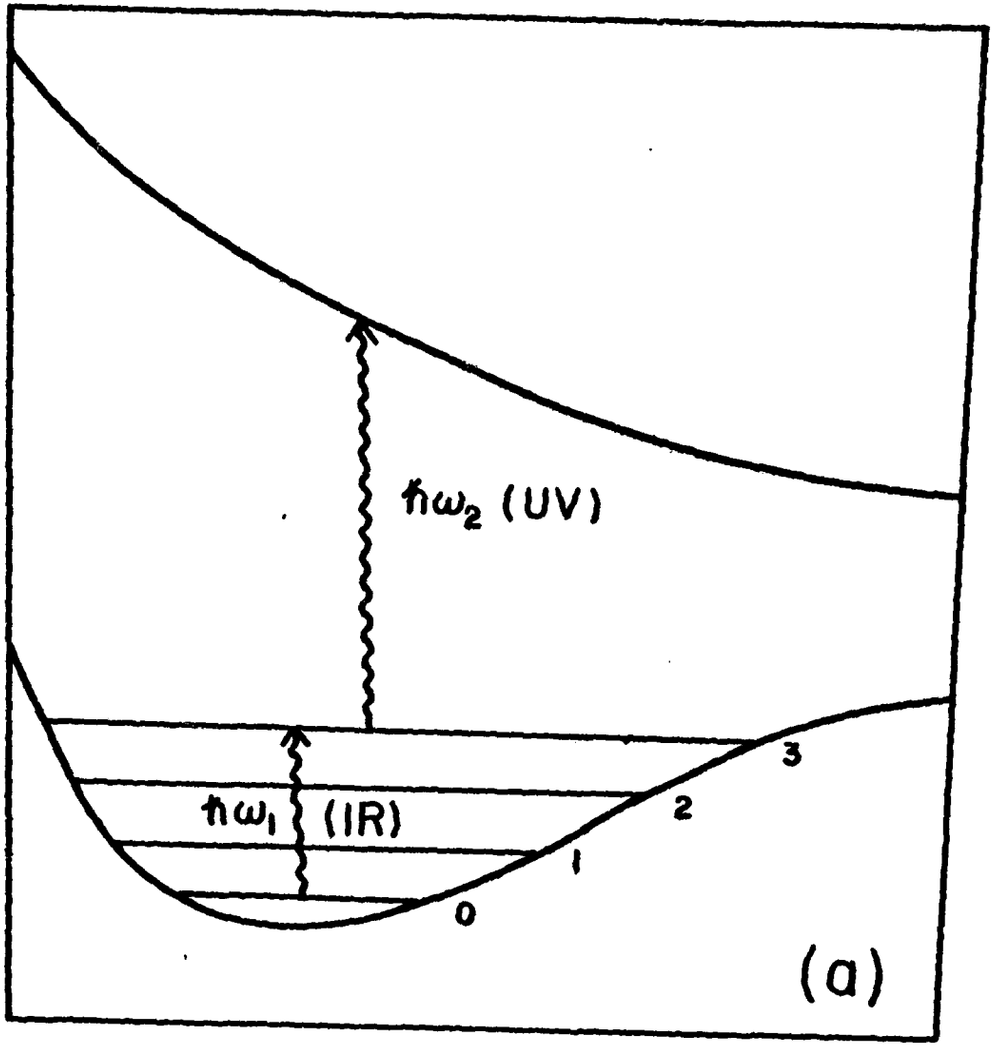
Fig. 1



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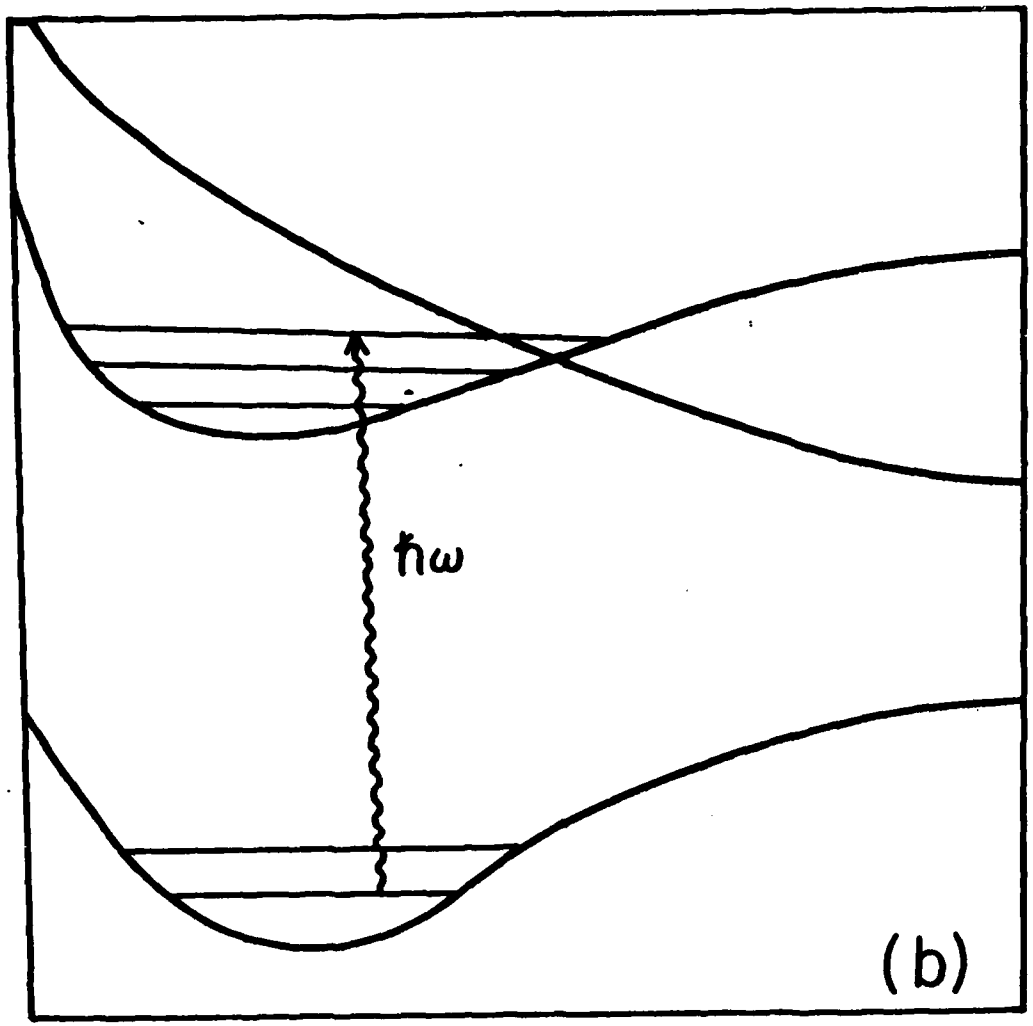

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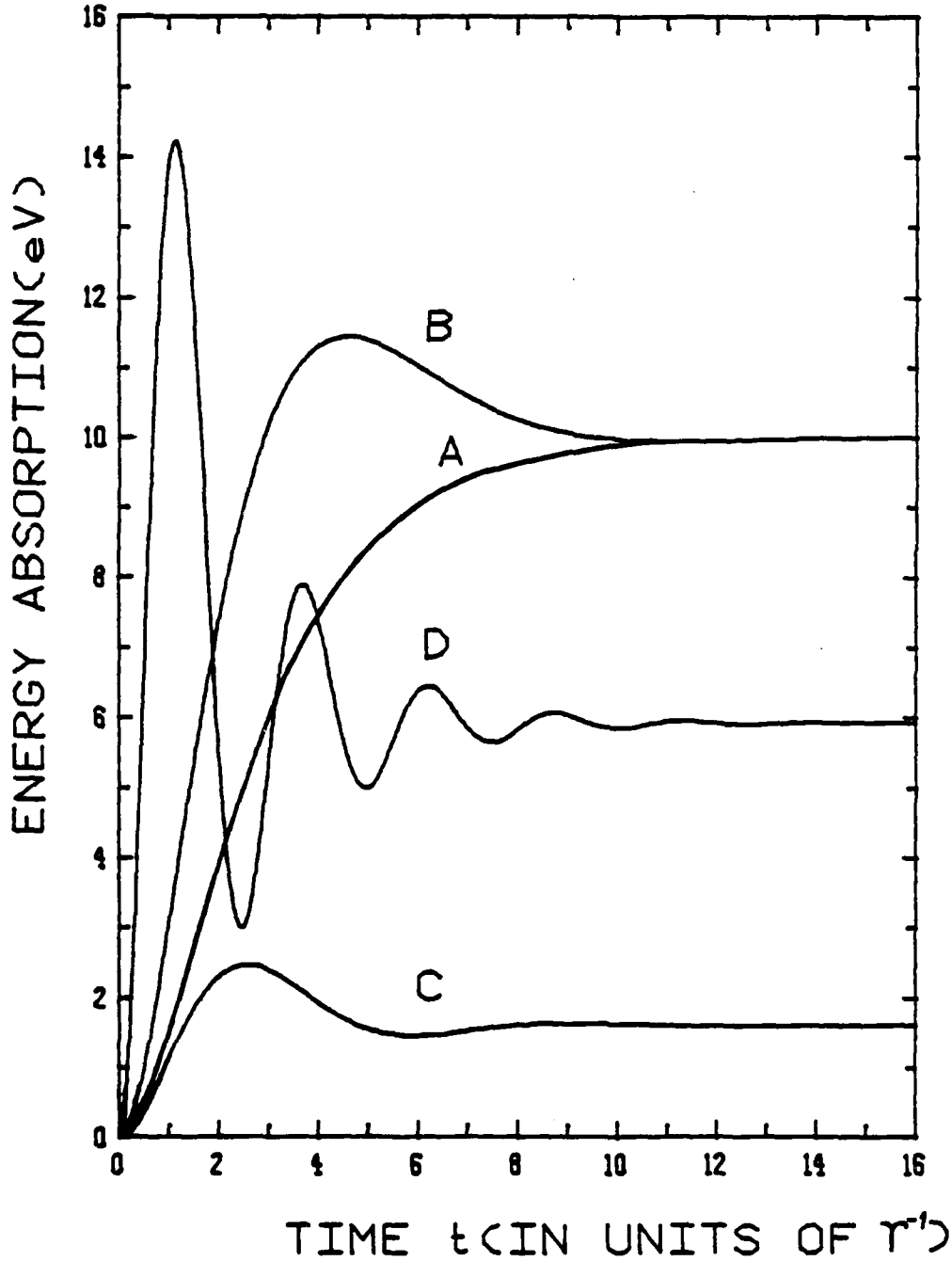
ENERGY ABSORPTION(eV)
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4
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8
10
12
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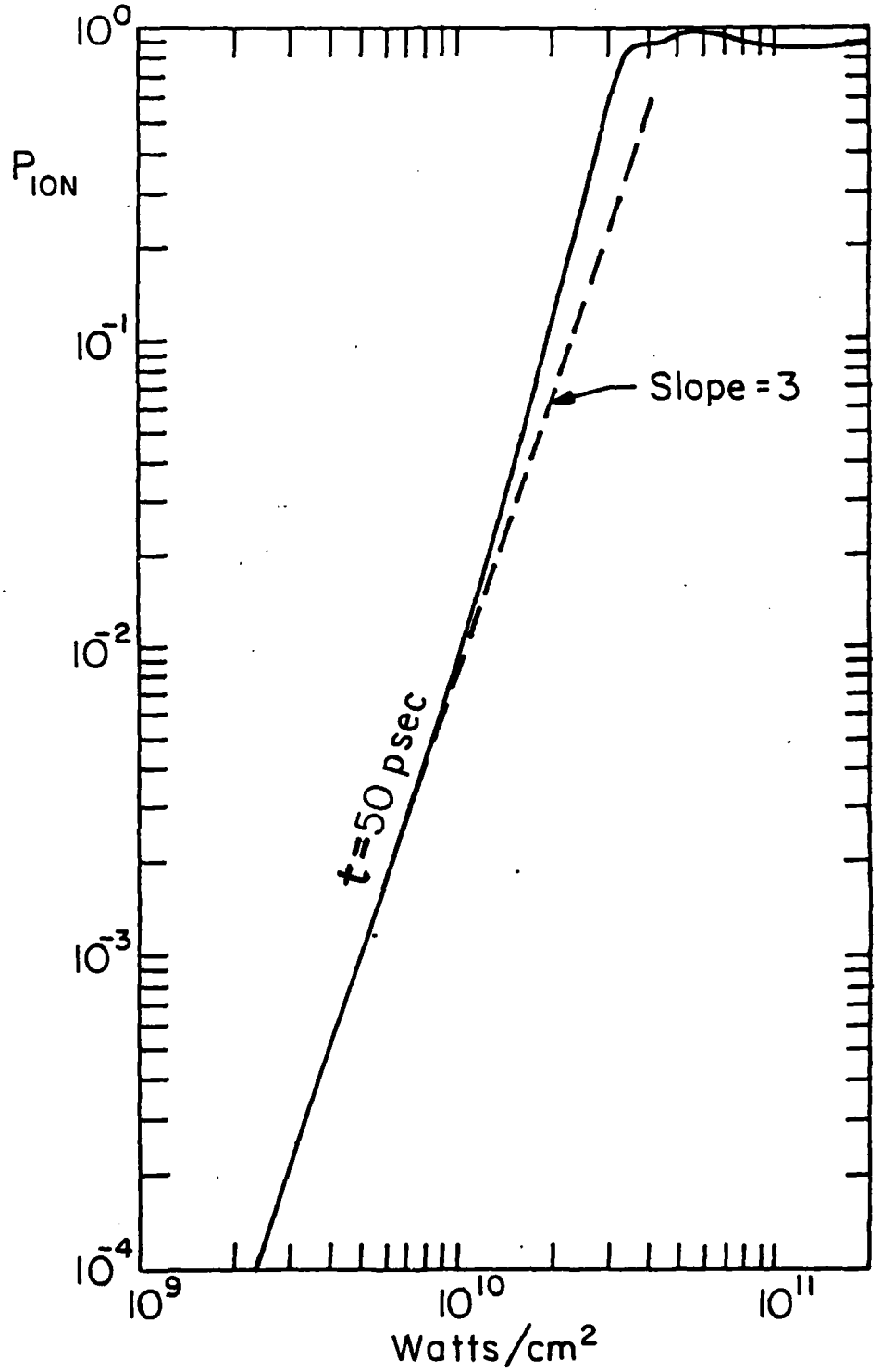
16
A
B
C
D

Fig. 3


10^0
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Watts/cm^2

Fig. 4.

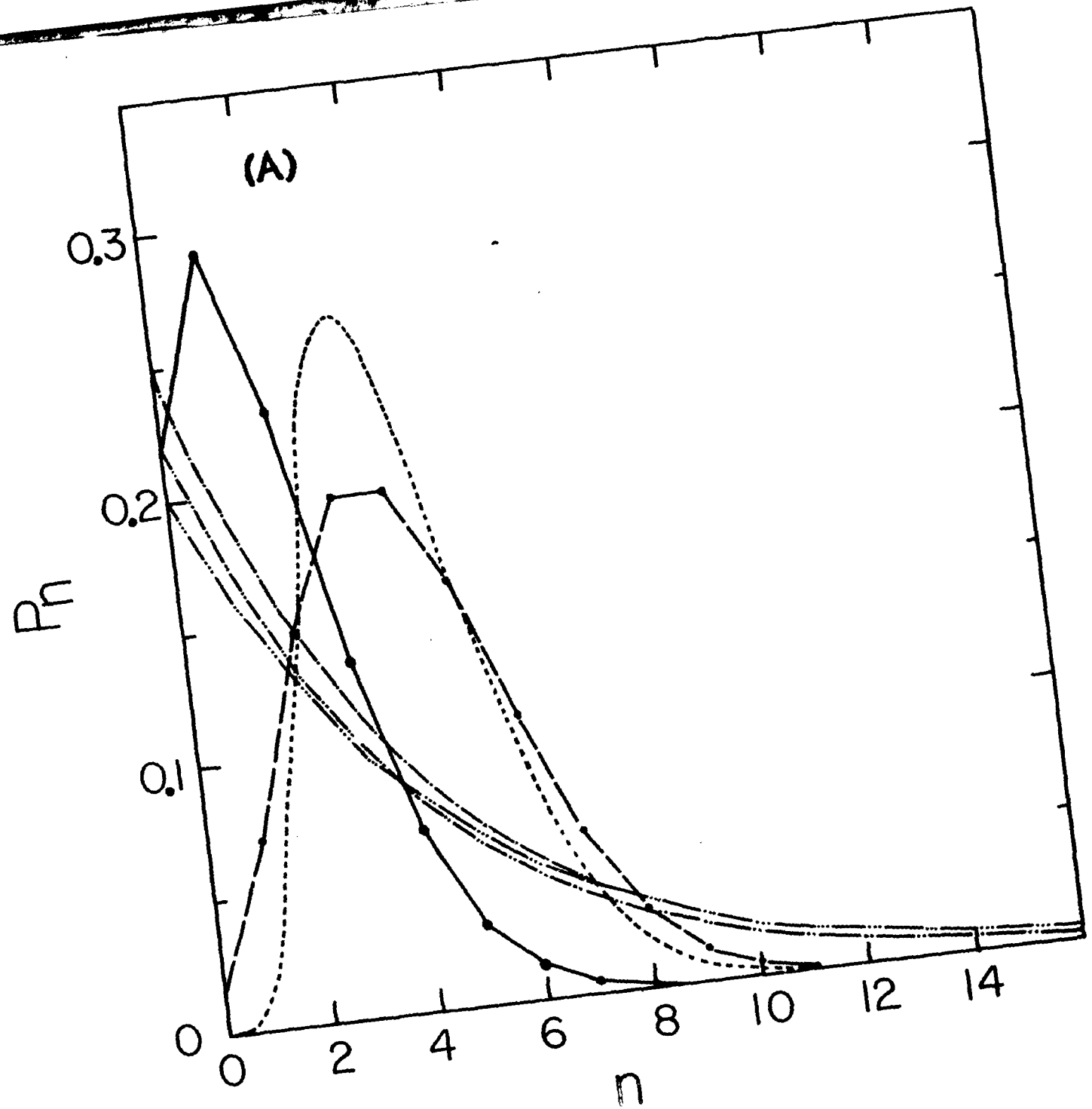
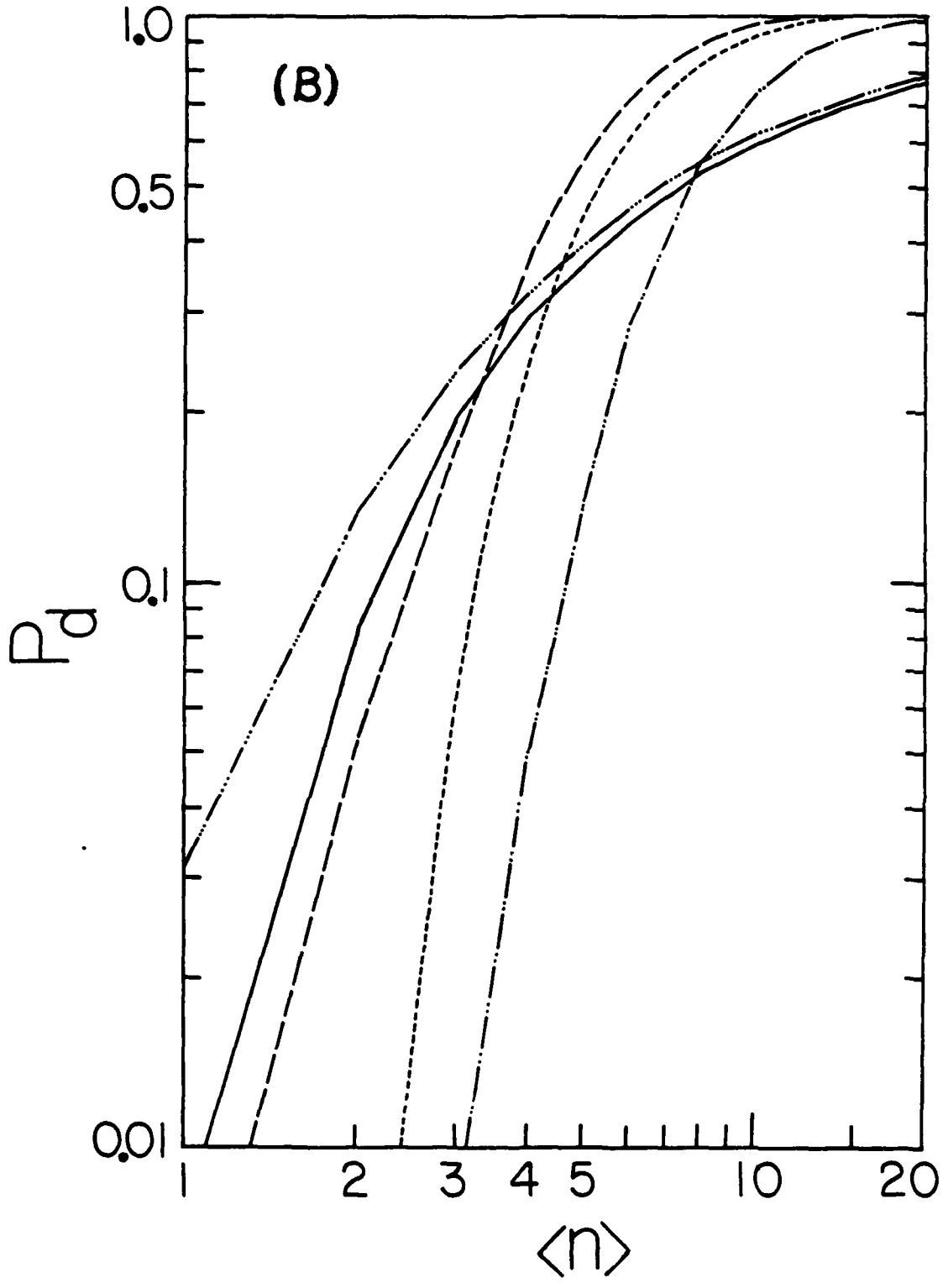


Fig. 5(A)



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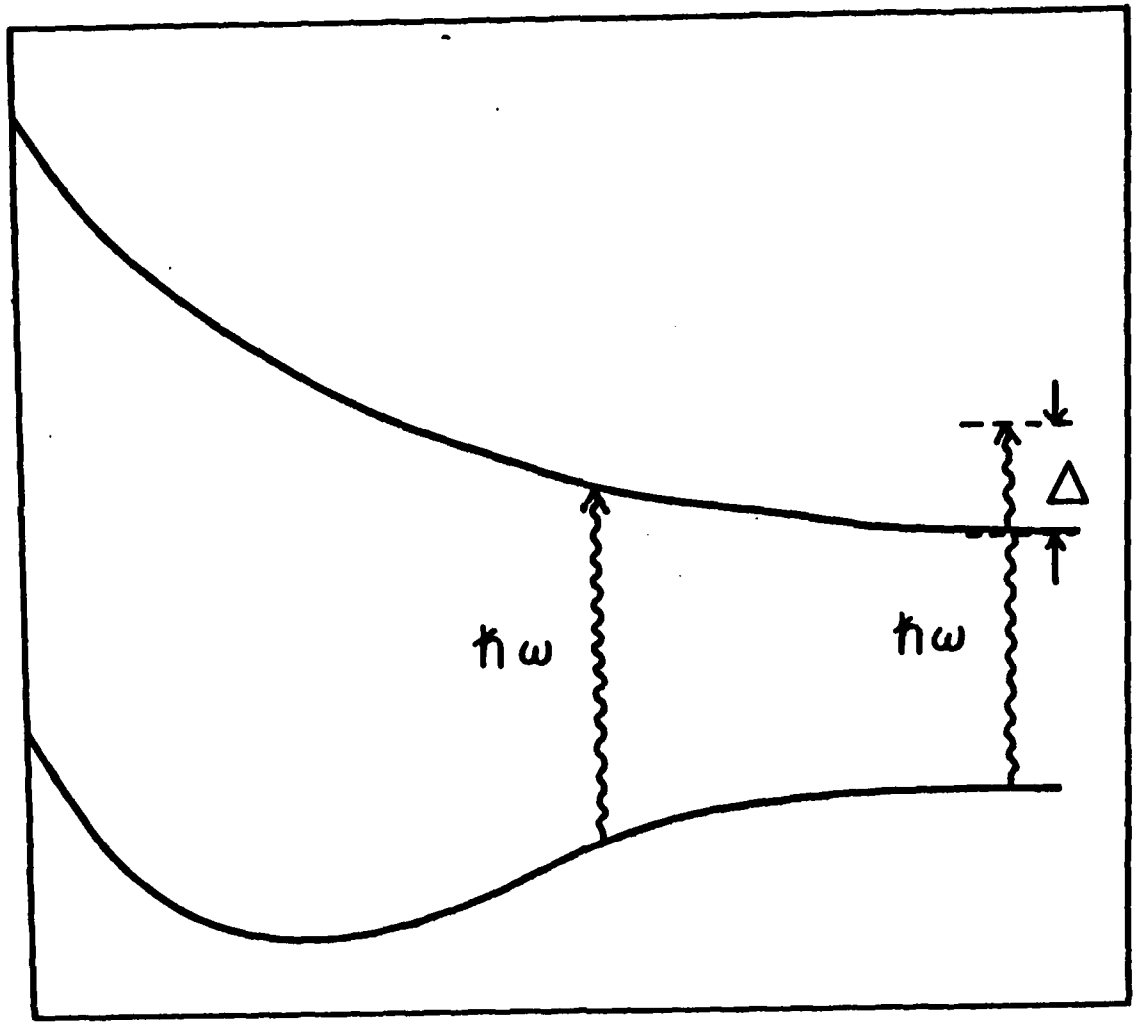
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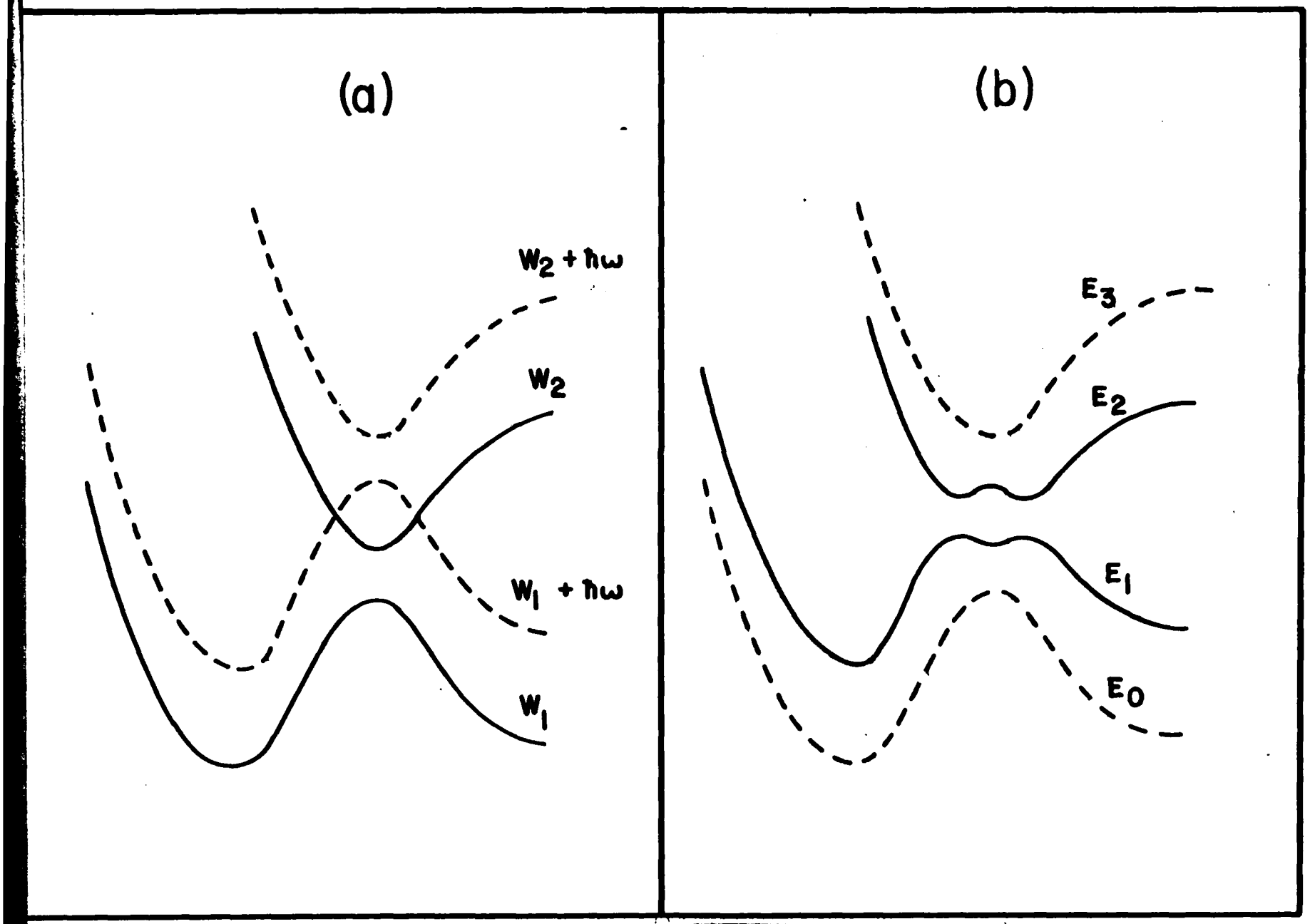
(a)
$W_2 + \hbar\omega$
W_2
$W_1 + \hbar\omega$
W_1
(b)
E_3
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E_1
E_0

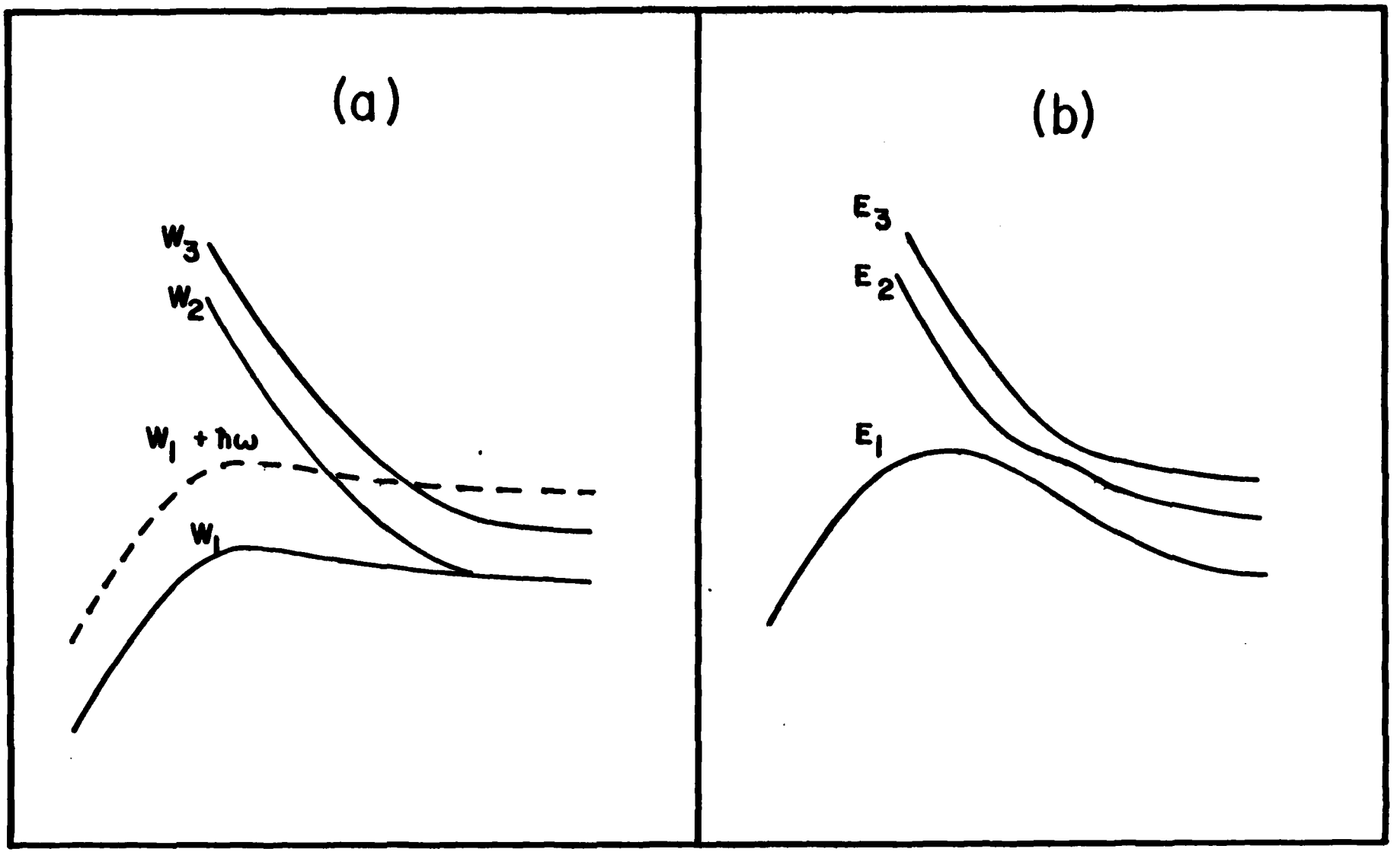


Fig 8

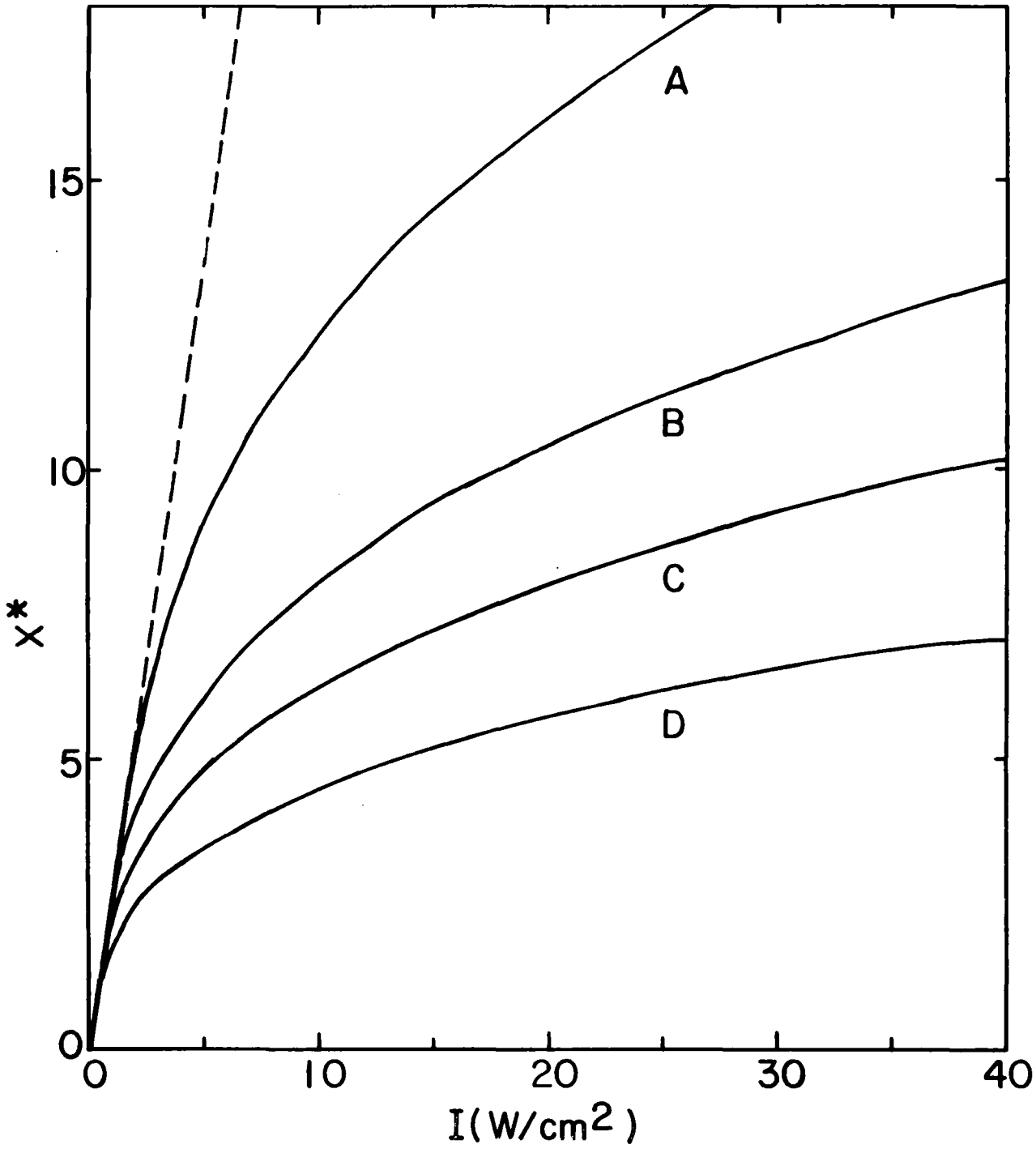


Fig. 9

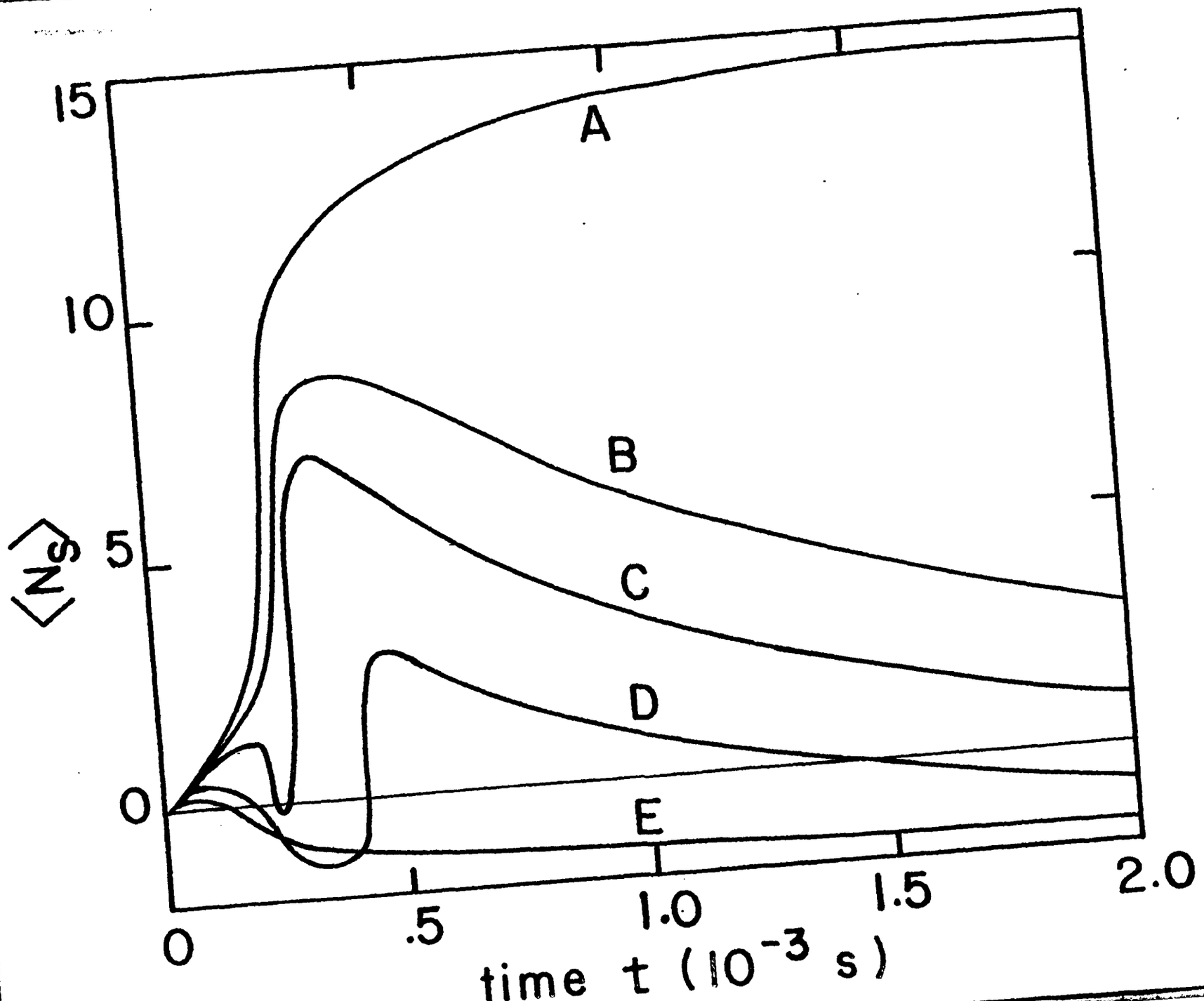
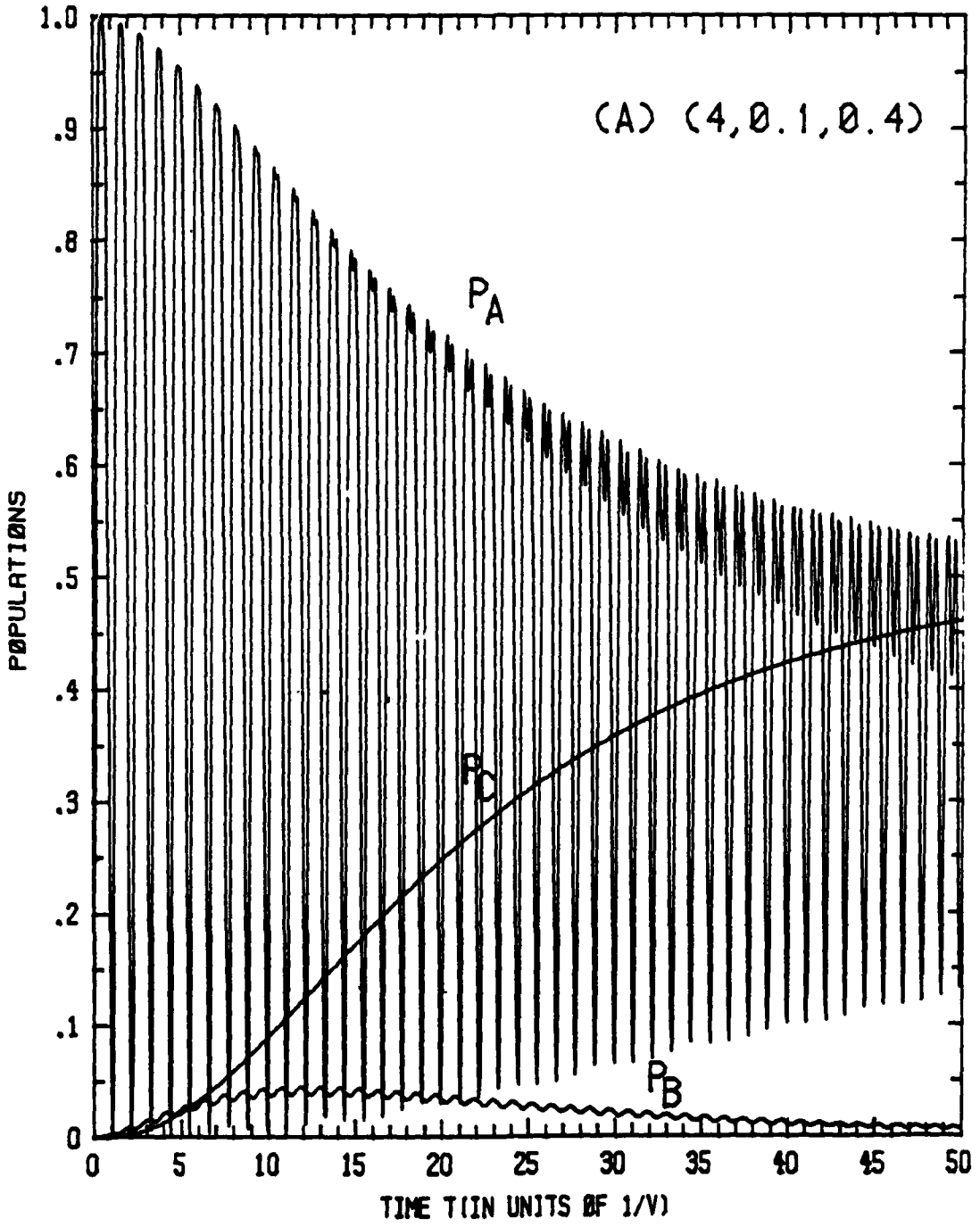


Fig. 10.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P_C
P_B
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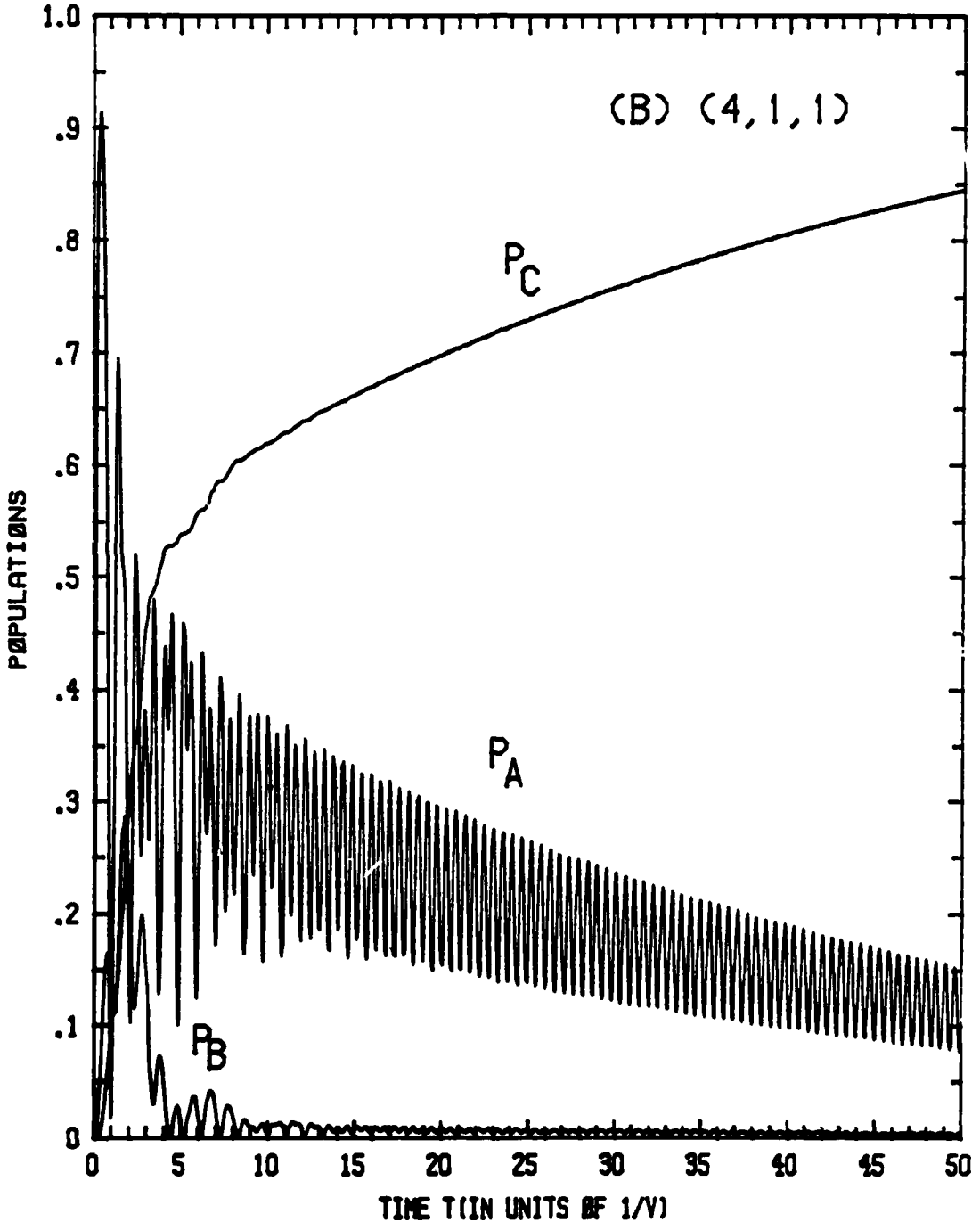
.8
.7
.6
.5
.4
.3
.2
.1
0
0
5
10
15
20
25
30
35
40
45
50

Fig. 11 (A)


(B) (4, 1, 1)
P_C
P_A
P_B
POPULATIONS
TIME T(IN UNITS OF 1/V)
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.7
.6
.5
.4
.3
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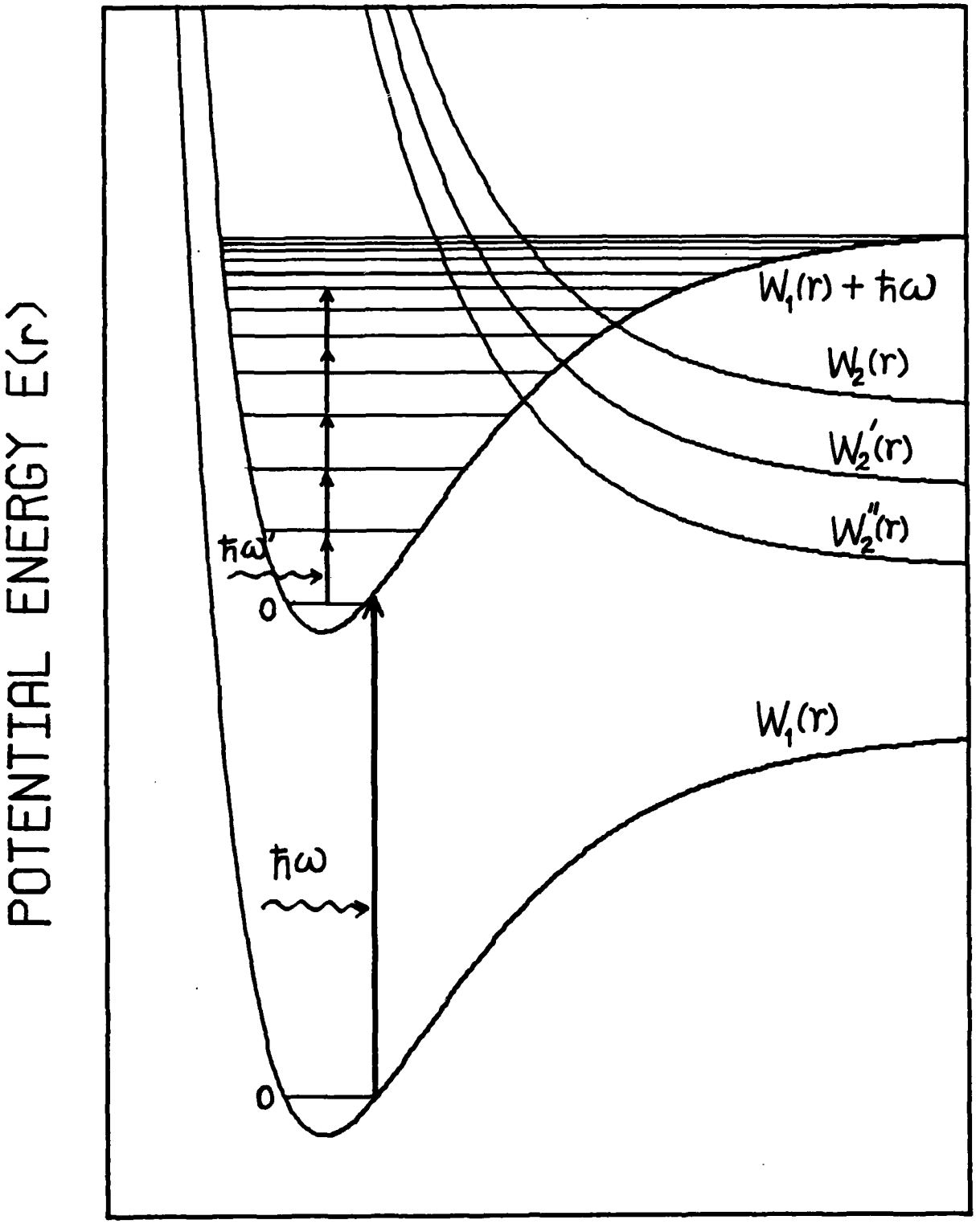
Fig. 11(B)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$W_1(r) + \hbar\omega$
$W_2(r)$
$W_2'(r)$
$W_2''(r)$
$\hbar\omega'$
0
$W_1(r)$
$\hbar\omega$
0
INTERNUCLEAR DISTANCE r

Fig. 12.

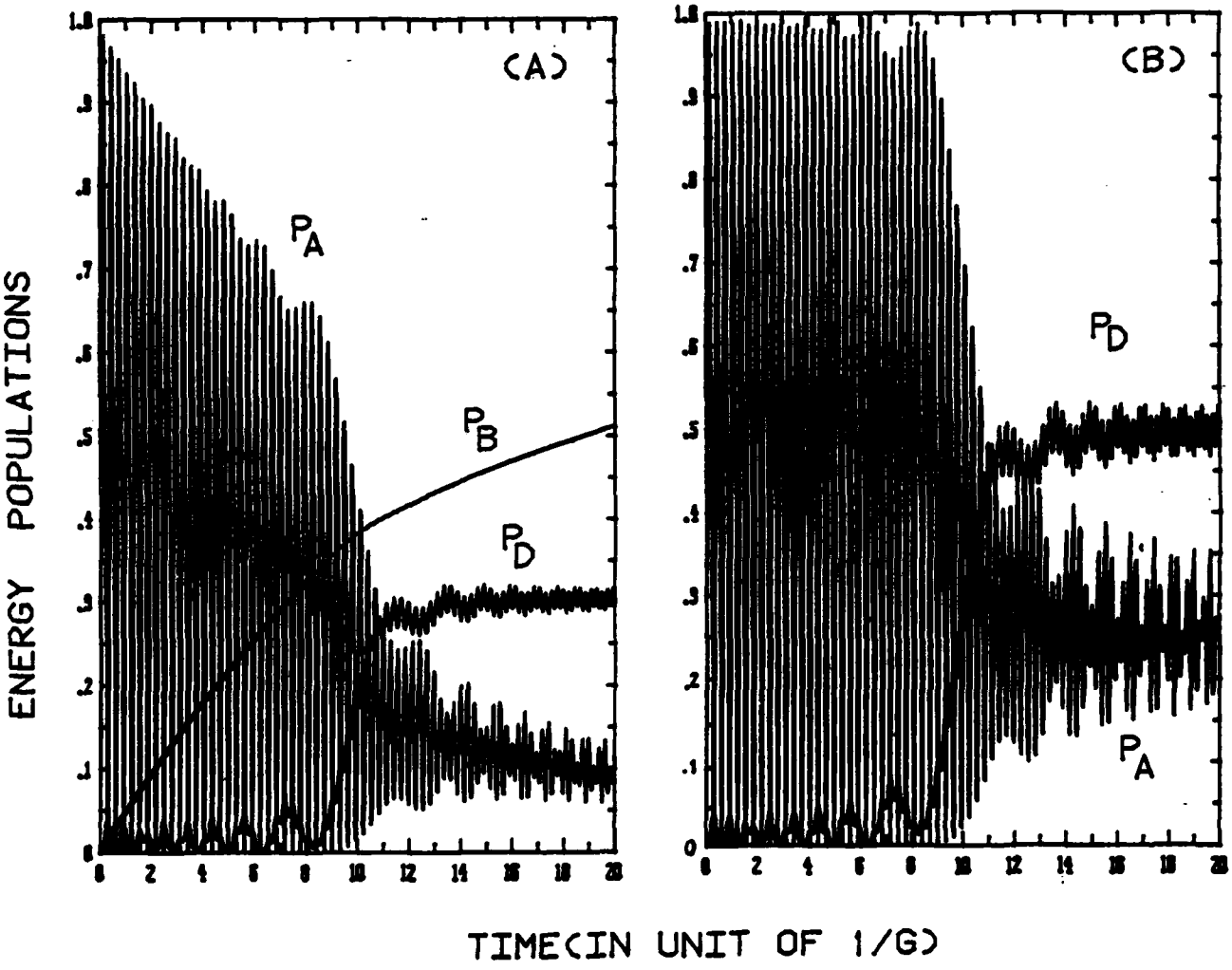
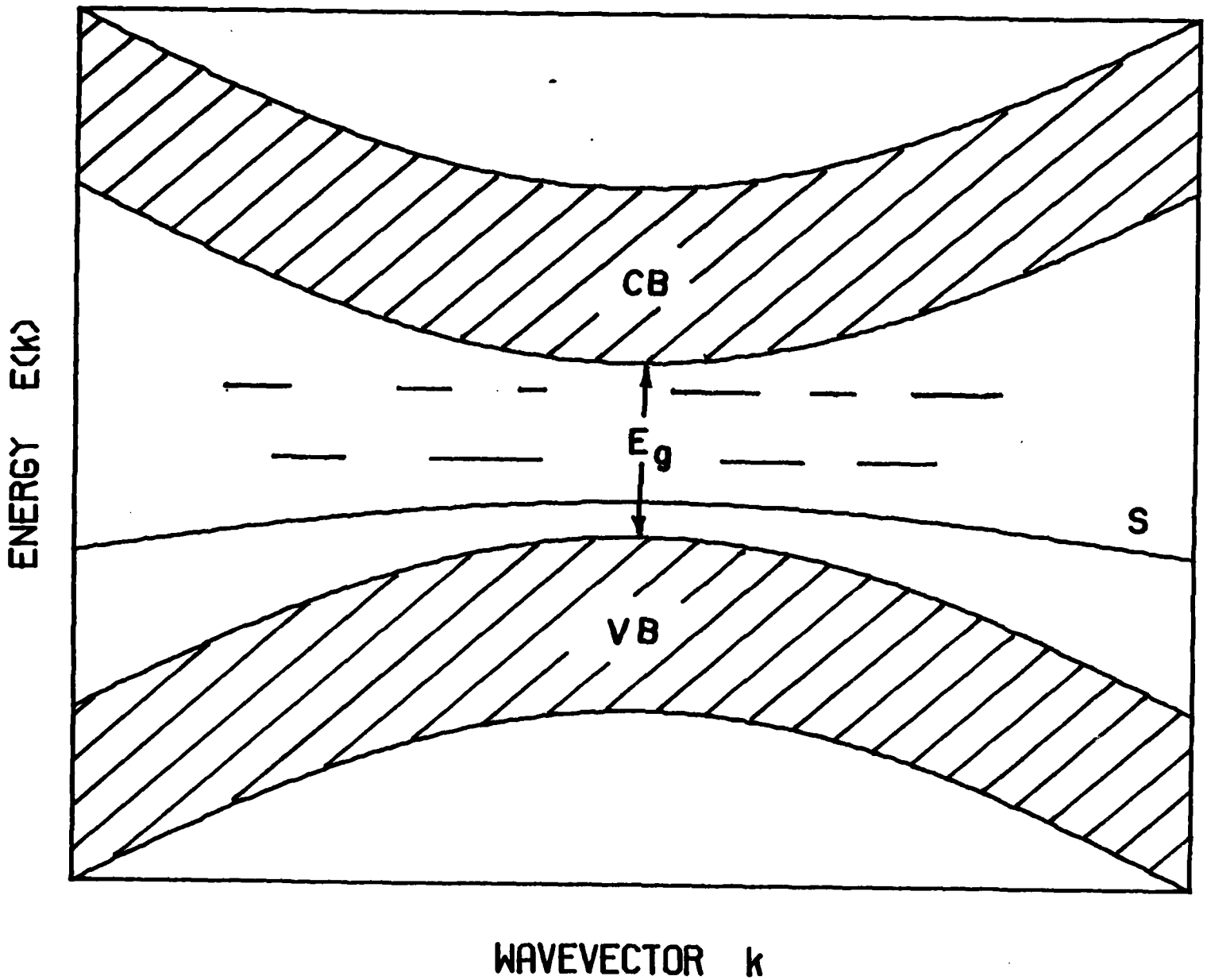


Fig. 13. (a) & (b)


ENERGY E(k)
CB
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VB
WAVEVECTOR k

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